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Degree Programme of Forest Products Technology

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MODELING OF CHEMICAL OXYGEN DEMAND (COD) IN A PAPER MILL

Master's thesis for the degree of Master of Science in Technology submitted for inspection,
Espoo, 17 March, 2014.

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Abstract of master's thesis

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Title of thesis Modeling of chemical oxygen demand (COD) in a paper mill

Department Department of Forest products technology

Professorship Environmental technology within process industry **Code of professorship** Puu-127

Thesis supervisor Prof. Olli Dahl

Thesis advisor(s) / Thesis examiner(s) M.Sc. Päivi Käki, M.Sc. Jouni Starck

Date 17.1.2014 **Number of pages** 96 **Language** English

Abstract

Stiffening environmental regulations and increasing public awareness has created pressure to develop better waste water management in the pulp and paper industry. Simulation software can serve the purpose of predicting and managing pollutant loads in process and effluent flows. Chemical oxygen demand (COD) is an indicator of the water cleanliness and is one of the parameters in environmental permits. All this makes COD an interesting parameter to simulate.

This thesis evaluates dissolved chemical oxygen demand (DCOD) which is a component of COD. Two DCOD balance models were created and evaluated in this thesis. Metso´s WinGEMS 5.3 simulation software was utilized to model the DCOD balances of one for thermomechanical pulping plant (TMP) and one for paper machine (PM). DCOD parameter is a computational parameter in the models because WinGEMS 5.3 does not contain COD related tools or gadgets. The basis in the COD modeling in this work was to set the DCOD values in the model points as close as possible to the measured values. This was accomplish hed by investigating the process units affecting on DCOD concentration (e.g., refiners at TMP) and then iterating the model point by point until acceptable accuracy was achieved. Accuracy of DCOD models was evaluated by help of "fitting curve" which is the graph of measured COD points, i.e. the target of the model. DCOD fitting curve fitted almost perfectly to the TMP model and reasonably well in PM model: The difference between measured and simulated values varied between 0 to 12 % in the TMP model and between 3 to 24% in the PM-model. Yield losses varied (compared to previous studies) between 25 - 100% and K-factors between 11 - 57% in the models. The values (yield and K-factors) should not be targeted since each mill has their unique characteristics thus COD model should be created based on measurement data not examples from literature. Hence literature comparison denotes the accuracy of the model only in magnitude scale. Collection of initial data was successful in the case of TMP but PM was drastically lacking information. Since the initial data is the key in modeling PM model is unreliable and requires further investigation whereas TMP model seems to resemble the reality well.

The technique of iteration produces an accurate model of the situation at measuring moment at the modeled mill if the initial data is sufficient. Hence created models, especially TMP, resemble reality well which was the purpose of this thesis. By the contrast, the models do not suit as they are to predict the change which is the greatest drawback of the models. Flow rate data of the purges should have been collected prior to simulation in order to connect all the output flows in relation to production instead of the fixed values utilized in the models. This is the greatest shortage in the models since the stagnant output flows of certain purges hinder the simulation capacity of future scenarios. The reason to the utilization of the fixed flows is the lack of flow rate data which is a problem especially in the old mills where flow meters are rare.

The results of this thesis indicate that the fitting curve iterative method is efficient and fairly accurate thus recommendable means to model COD in paper mills. Close attention needs to be paid on investigating sufficient amount of initial data. Firstly, DCOD analysis must be performed on several points of the process and secondly, information on output water trends needs to be gathered in order to maintain the simulation capacity of the created model.

Keywords Dissolved Chemical oxygen demand (DCOD), Chemical oxygen demand (COD), simulation, WinGEMS, thermomechanical pulping plant, paper mill

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Diplomityön tiivistelmä

Tekijä Eeva Ronni

Työn nimi Kemiallisen hapenkulutuksen (COD) mallintaminen paperitehtaassa

Laitos Puunjalostustekniikan laitos

Professuuri Prosessiteollisuuden ympäristötekniikka **Professuurikoodi** Puu-127

Työn valvoja Prof. Olli Dahl

Työn ohjaaja(t)/Työn tarkastaja(t) DI Päivi Käki, DI Jouni Starck

Päivämäärä 17.1.2014 **Sivumäärä** 96 **Kieli** Englanti

Tiivistelmä

Tiukentuvat ympäristövaatimukset vaativat tehokkaita menetelmiä ja tapoja hallita jätevesiä sellu- ja paperiteollisuudessa. Mallintaminen on eräs kustannustehokas keino hallita ja ennustaa teollisuuden jätevesi- ja prosessivesikuormia. Kemiallinen hapenkulutus (COD) on tehtaille merkittävä parametri, sillä se kuvaa jäteveden puhtautta. COD on myös ympäristöluvissa määritelty parametri täten mielenkiintoinen mallinnuskohde.

Tässä diplomityössä mallinnettiin COD:n liukoinen osa (DCOD) kuumahierrelaitoksen (TMP) ja paperikoneen (PM) prosesseissa. Työ tehtiin Metson WinGEMS 5.3-ohjelmistolla. DCOD sisällytettiin malleihin laskennallisena parametrina, sillä WinGEMS 5.3 ei sisällä COD:n mallintamiseen liittyviä työkaluja. COD-mallinnuksen peruslähtökohta oli iteraation keinoin saada malli vastaamaan mittausdataa. Lähdekirjallisuuden perusteella valittiin COD-konsentraatioon vaikuttavat prosessin osat (esim. jauhimet TMP:llä), jonka jälkeen kohta kohdalta mallia ohjattiin kohti haluttua tarkkuustasoa. Iteraation onnistumista ja työn tarkkuutta arvioitiin nk. kiinnityskäyrän avulla. Kiinnityskäyrä on DCOD:n mittausdatasta tehty kuvaaja eli samalla mallin tavoitetaso. TMP-malli kiinnittyi käyrälle hyvin ja paperikoneen malli kohtalaisesti: Mitatut ja mallinnetut arvot vaihtelivat TMP-mallissa 0 - 12 % välillä ja PM-mallissa 3 – 24 %. Malleista laskettiin myös saantohäviö sekä K-arvot, joita verrattiin aiempaan tutkimustietoon. Saantohäviöt poikkesivat kirjallisuusarvoista 25 – 100 % ja K-arvot 11 – 57 %. Saantohäviöitä ja K-arvoja tarkasteltiin lähinnä suuruusluokaltaan, eikä niitä yritetty saada vastaamaan kirjallisuuden esimerkkejä, sillä jokainen laitos on yksilöllinen. COD-malli tulee perustua mittausdataan, eikä kirjallisuusesimerkkeihin. Rakennetuista malleista TMP-malli onnistui PM-mallia paremmin. TMP:lle lähtötietoa oli riittävästi, kun taas paperikoneen tapauksessa informaation keräämisessä epäonnistuttiin. Tästä johtuen PM-malli on epäluotettava ja vaatii lisätutkimusta.

COD:n iteratiivinen mallinnustekniikka näyttää tuottavan tarkan kuvan mallinnettavan tehtaan mittaushetken tilanteesta, mikäli lähtötiedon taso on riittävä. Sen sijaan, tässä tutkimuksessa rakennetut mallit eivät sovi ilman muutostöitä tulevaisuuden tilanteiden simuloimiseen. Molemmissa malleissa osa ulos virtaavista vesivirroista on mallinnettu virheellisesti muuttumattomiksi eikä niitä ole sidottu tuotantoon. Tästä syystä tuotannon muuttuessa virtausarvot eivät päde. Syynä muuttumattomien virtausten käyttöön mallissa oli virtaamatiedon puute.

Tämän diplomityön tulokset osoittavat, että iteratiivinen kiinnityskäyrämetodi on tehokas ja melko tarkka tapa mallintaa COD:ta paperitehtailla. Ehdotonta tarkkuutta tulee käyttää aineiston keräämisen yhteydessä. DCOD on mitattava useista prosessin kohdista ja lähtevistä vesivirroista tulee kerätä tarpeeksi tietoa. Näin ollen mallien kyky muutoksen havainnollistamiseen säilyy.

Avainsanat: Liukoinen kemiallinen hapenkulutus (DCOD), kemiallinen hapenkulutus (COD), WinGEMS, mallinnus, kuumahierre, paperitehdas

Contents

ACKNOWLEDGEMENTS

I offer my gratitude to my supervisor, Profesor Olli Dahl, and instructors, Päivi Käki and Jouni Starck, who have guided me to this point, the Grande finale. I give my sincere thank you to Mikko Martikka who has supported me throughout my degree with his patience and knowledge whilst allowing me to find my own path.

Special thanks to Elina Kalliola, Heikki Lotti, Markus Jaanu, Jean Balac, Lauri Pekkanen, Tomas Blomberg and Martin Taxacher who offered their advice and insight when modeling got too steep. For Tom Lind, Päivi Käki, Liisa Pelkonen and Petri Söderberg I would like to express my deep gratitude for mentoring and taking me as one of yours right from the start.

Finally, I want to thank Kaarina and Niko who provided much-needed encouragement on the home stretch. Heartily thanks to Jenny, Milja, Outi, Pilvi, Sari and Irena who made my days and grew up with me. I give sincerest gratitude for Hanna-Mari, Essi and Laura for their friendship and for keeping my thoughts versatile. Greatest thanks to Jukka with whom I have simultaneously my head in the clouds and toes on the ground. Thank you for your endless love and support.

ABBREVIATIONS

BOD	Biological oxygen demand
CD	Cationic demand
COD	Chemical oxygen demand
DAF	Dissolved air flotation
DCOD	Dissolved chemical oxygen demand
DCS	Dissolved and colloidal substances
DIP	Deinked pulping plant
MBR	Membrane bioreactor
MEEP	Multi-effect evaporation plant
MVR	Mechanical vapour recompression
PM	Paper machine
SBR	Sequencing batch reactor
TC	Total carbon
TMP	Thermomechanical pulping plant
TOC	Total organic carbon
UASB	Upflow anaerobic sludge blanket reactor

1 INTRODUCTION

Environmental awareness has increased in recent years in the pulp and paper industry due to stiffening regulations (e.g. IE-directive), diminishing water resources, image upgrading issues, customer demands and increasing waste disposal costs. Pulp and paper sector is considered as water intensive field of industry thus need of cost-efficient water contaminant management is required. Modeling software offers an efficient tool for predicting changes in water contamination and flow rates.

This thesis discusses on chemical oxygen demand (COD): content, removal and control in paper mill process waters. The literature part studies COD in detail in the case of thermomechanical pulping plant (TMP), deinking plant (DIP) and paper machine (PM) in the light of reducing water consumption or even closed water cycle. The experimental part describes in detail the steps how to reach an accurate model but also describes in depth the challenges and poor decisions, those to be avoided in the future. This work is continuation of the thesis of Henna Kankare. Kankare noticed in her work that creating equipment based COD-parameter is unachievable due to impassable challenges in COD-analysis of high consistency streams. In addition generalization of equipment COD-parameters would have been unrealizable due to the uniqueness of each mill, process water qualities and equipment characters. Hence this work started developing COD-model strongly relying in *overall COD-trend* in each department.

This work was part of Pöyry´s project considering a paper mill in Central Europe which provided the base and data for the study. A whole mill balance including the pulp plants, all the paper machines and the waste water treatment plant was prepared but this thesis studies the modeling procedure of the thermomechanical pulping plant and one of the paper machines in detail. The needs of the client mill were specified during the process and COD characterization of process waters was rejected. Lighter specification (hard COD) was selected instead of studying the process waters in detail. Hard COD was analyzed in 10 points to explore the non-biodegradable part in waters. This information is relevant if treatment methods are focusing on biological treatment. Due to earlier needs COD characterization is studied in the literature part and only dissolved COD is modeled in the experimental part.

The experimental part comprises of two goals. The first is to create a reliable COD balance and the second is to subject the *modeling procedure* to investigation. The transparency of COD-modeling and reviewing the process is important to improve the model accuracy and the efficiency of the modeler. Attention in process engineering focuses frequently mainly on the main product, i.e. paper, that claims more efficient procedures to study other than process related components, such as, COD. This is emphasized in situations where wastewater is not the key subject but environmental parameters are highly valued. When the procedure is clear and simple COD-balance can be obtained along other balances thus increasing the environmental information.

Pöyry ordered this thesis to increase their knowledge on COD formation, management and modeling. Four research questions derived from the purpose:

I. *What is COD in the process waters of TMP, DIP and paper machine?*
II. *How to remove and control COD in these processes?*

Literature part answers to questions I and II. Initially the client mill pursued holistic knowledge on their process waters and waste waters hence approach of COD characterization is studied in this thesis. Due to detailed starting point COD removal is discussed in COD component level in chapters 4 and 5.

III. How to model COD?

The aim was to create a reliable COD-model of a paper mill and document the procedure from data acquisition to completed model.

IV. How to enhance COD modeling

Pöyry required information on the COD modeling procedure: how to repeat the modeling of COD in other paper mills and what were the challenges in the modeling of COD. Documentation of the modeling procedure creates a fruitful base to repeat and further develop the procedure in Pöyry.

1.1 The structure of this thesis

Figure 1 introduces the structure of this thesis. Introduction describes the context in which the thesis was performed, the research problems, objectives, scope and the structure of the study. The purpose of chapter 2 was to bind the study in to larger entity thus introducing the reader the background information. Chapters 3 to 5 answer to the research questions I and II. Chapters 6 to 8.2 response to the research question III and 8.3 to the question IV. Conclusions and recommendations state the most important results and recommendations for further research. Finally, summary concludes the used materials and methods, the results and revisits the recommendations and conclusions of this thesis.

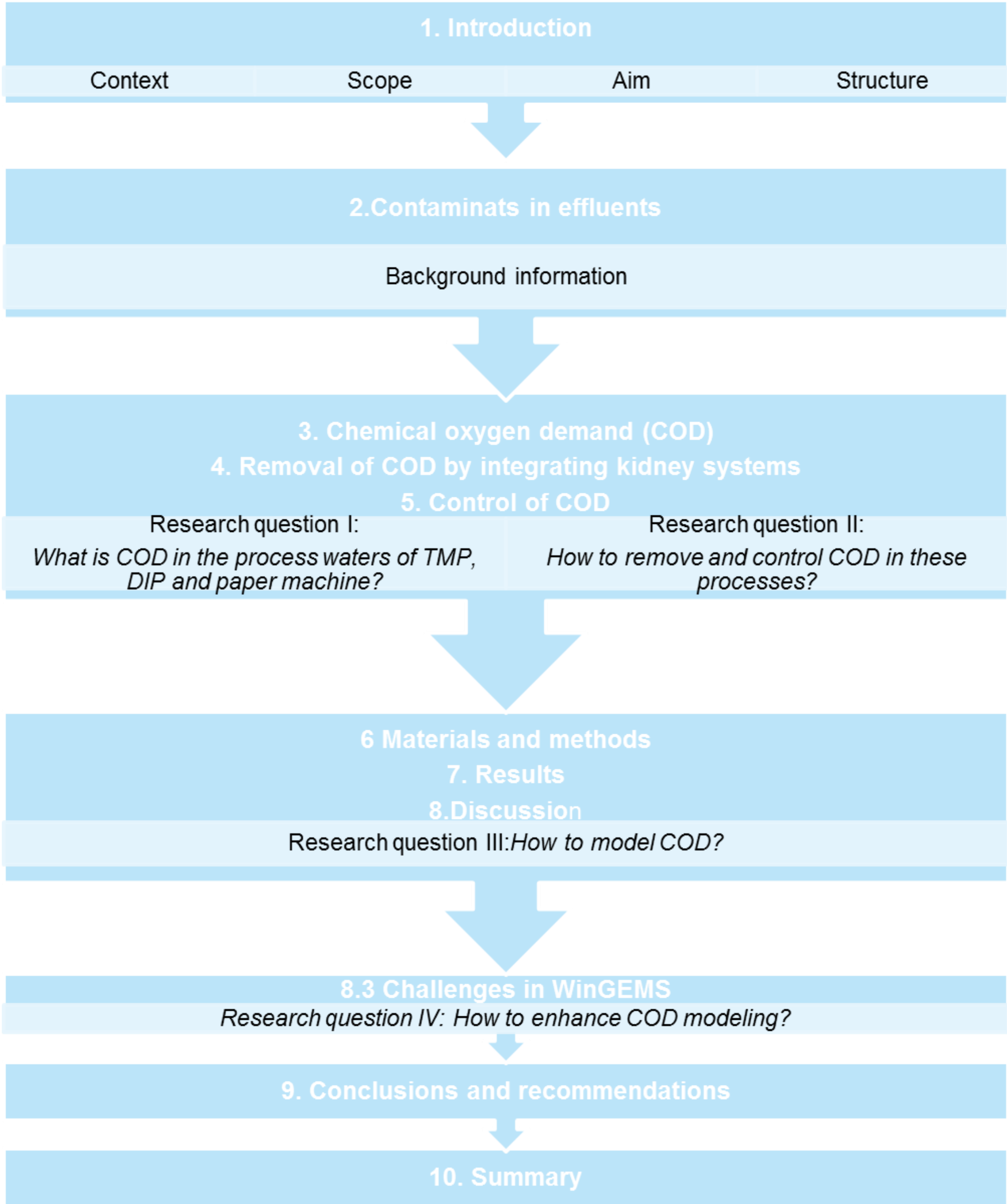

Figure 1 The structure of this thesis

2 CONTAMINANTS IN EFFLUENTS

2.1 Dissolved and colloidal substances (DCS)

Dissolved and colloidal substances (DCS) are a sum of three components: i) polyelectrolytes, ii) other dissolved components and iii) very small (< 1 µm) dispersed particles present in process waters. These substances are troublesome in papermaking process due to the adverse impacts on paper quality and paper machine operations. Sources of DCS include wood derived substances, components from waste paper, coating materials and chemicals added to paper making process (e.g. dyes, dispersants) hence TMP, DIP and paper mills are all struggling with accumulation of DSC especially when water consumption is reduced. (Hubbe et al. 2012).

Typically, dissolved substances consist of ions and molecules that comprise less than 0.1 µm diameter, e.g., soluble polyelectrolytes (such as, hemicelluloses, pectins and lignin fragments). Colloidal substances typically consist of dispersed particles ranging from 0.1 to 1 µm, e.g., wood pitch, latex (present in the process waters of coated grades) and microfines. (Hubbe et al. 2012). COD load is caused mainly from substances smaller than 0.2 µm, which creates DCS a key factor when reducing and controlling COD (Miranda et al. 2008).

2.2 Anionic trash

Negatively charged dissolved and colloidal substances are called anionic trash. Main contributor of anionic trash is wood derived components since those contain carboxyl acid groups that dissociate to their negatively charged carboxylate form in the pH conditions prevailing in paper machine systems, TMP and DIP plants. The term *charge demand* is frequently used in research and it is used to express the amount of high-charge polyelectrolyte needed to *neutralize* the ionic charge of DCS. (Hubbe et al. 2012).

2.3 Pitch

Wood pitch, i.e., lipophilic extractives, such as fatty and resin acids, sterols, steryl esters, and triglycerides, cause pitch problems during pulping, bleaching and at the paper machine. Certain components, especially stearic acid (a fatty acid), abietic acid (a resin acid), sitosterol (a sterol), sitosteryl linoleate (a steryl ester) and trilinolein (a triglyceride) are responsible for fouling and quality problems in paper making. The lipophilic extractives are released from the parenchyma cells and from softwood resin canals thus forming colloidal pitch. Colloidal particles deposit in pulp and on machinery or remain suspended in the process waters which results in low pulp quality, environmental problems and can cause the shutdown of mill production. Pitch causes additional costs due contaminated pulp and pitch control additives. (Gutiérrez et al. 2001).

2.4 Stickies

Stickies are organic contaminants derived from wood pitch, process chemicals (coating formulations, sizing agents, wet-end additives, etc.), and recycled paper derived contaminants (hot melts, contact adhesives, coating binders, starches, ink binders etc.). Stickies deposits consist of a mixture of acrylates, ethylene vinyl acetate, polyvinyl acetate, polyacrylates, styrene rubber, etc. Stickies create runnability problems and increase downtime due to breaks hence additional cleaning is required. Stickies are hydrophopic, tacky and deformable and possess low surface energy. Stickies are classified according their size to: suspended (20-100 µm), dispersed (1-25 µm), colloidal (5-0.01 µm) and dissolved (< 0.01µm) but this alone is insufficient method of segregation thus characterization according the source is needed. Stickies originated from repulping are termed native or primary stickies and stickies that precipitate due to the changes in pH, temperature or chemical environment are termed potential or secondary stickies. Organic DCS, originated from adhesives, printing inks, coating binders, starches, deinking chemicals and wood extractives are responsible for secondary stickies in deinking process. (Blanco et al. 2007;Miranda et al. 2008)

2.5 Inorganic salts

Calcium, sulphates, chlorides, silicates, iron, manganese, and copper salts are commonly found in papermaking process. They are nuisance for the process due to their ability to cause corrosion, odor, scaling and reduce the efficiency of additives. (Berard 2000)

2.6 COD, BOD, TOC and K-value

COD, BOD and TOC indicate all indirectly waste water quality. COD and BOD indicate the oxygen demand and TOC the total organic bound carbon. Waste water quality can be quantified with these parameters and rations describing waste water characters. Waste water analysis COD, BOD, TOC are all sum parameters. In other words they comprise of several oxygen consuming components. Oxygen demand is an important criterion in waste water management since it has a direct impact on the oxygen level of the receiving water course. Table 1 represents comparisons of rations of various parameters used to characterize waste water. (Tchobanoglous et al. 1991. p.97)

K-value describes the washing efficiency (see formula 3). K-values below 1 indicate that concentration of COD is lower in the pressed fiber mat than in the filtrate. Consequently, vice versa for K-values over 1. (Lappalainen 2008).

Table 1 Rations of COD, BOD and TOC of various waste waters (Tchobanoglous et al. 1991. p.97)

Type of waste water	BOD/COD	BOD/TOC
Untreated	0,3-0,8	1,2-2
After primary settling	0,4-0,6	0,8-1,2
Final effluent	0,1-0,3	0,2-0,5

3 CHEMICAL OXYGEN DEMAND (COD)

Chemical oxygen demand (COD) is a sum parameter that indirectly reflects the total concentration of oxidizable organic and inorganic material present in the effluent sample (Sankari 2004). In other words COD is a measure of dissolved and colloidal substances that can be chemically dissolved (Schabel et al. 2010 p.493). Laboratory tests determine indirectly the oxygen demand by measuring the amount of oxidant consumed by the effluent sample thus COD measures the chemical decomposition of pollutants present in effluent. Strong oxidizing agents such as potassium permanganate or *currently* mainly adopted potassium dichromate is used in the determination of COD due to its better capability to oxidize a wide variety of organic substances almost completely to dioxide and water. (Sawyer et al. 2003, p. 625).

COD should not be used to determine organic load as it is in process waters since addition to organic substances some inorganic components may be oxidized as well during the COD determination (Sawyer et al. 2003, p. 625). Evaluating water contamination based on COD determination is not entirely problem free since COD value does not provide information on any specific components present in the effluent. Hence evaluation based on COD can be difficult since some components, such as methanol, causes great amount of COD but are not important environmentally or process wise (Sankari 2004). Traditionally COD parameter has been used to measure dissolved components and fine particles in paper industry waters but due to increased knowledge regarding the behavior of components more precise methods, such as 5-component analysis of COD, has emerged (Lenes et al. 2001). Despite of the disadvantage coarse sum parameters are valuable in controlling process conditions in wet end (Holmbom and Sunberg 2003) and COD is rather quick estimate for oxygen consumption and suits well in the battery of water analysis.

3.1 Characterization of COD

Optimal removal of COD and technical realization highlight the importance of knowing the characteristics of waste waters. Identification of COD fractions and qualitative knowledge enable to adopt the technical solutions with maximum benefit that leads to more efficient and cost-effective water treatment, optimal operation and empowers modeling of future scenarios (Puhakka 2001). COD can be fractionized by several approaches but in this thesis 5-component system is presented.

The most important component groups to analyze are carbohydrates, lignin, extractives, lignans and low molecular weight acids since they sum up to 75-90% of the COD and TOC values in TMP process waters. Consequently, wastewater can be characterized by chemical analyses by using 5-component system. (Lenes et al 2001). Theoretical COD varies between the components. Table 2 presents COD-factors, i.e., theoretical COD amounts by components.

Table 2 Theoretical values of COD and TOC per unit mass (Lenes et al. 2001)

Compounds	COD factor	TOC factor
Carbohydrates	1.2	0.42
Extractives	2.7	0.80
Lignans	1.9	0.66
Lignin	1.9	0.66
Acetic acid	1.1	0.40
Lactic acid	1.1	0.40
Methanol	1.5	0.37

3.1.1 TMP process waters

The main and hence most important organic constituents in TMP wastewaters are carbohydrates, lignin, extractives (e.g., fatty and resin acid and sterols), low molecular weight compounds (e.g., acetic acids) and lignans (Lenes et al. 2001). Hence COD load can be characterized accordingly since the dissolved organic compounds are mostly responsible for COD load. The organic material circulating in TMP process waters is well characterized in several studies since organic components have a severe effect on process efficiency and paper quality. In the study of Wågberg and Ödberg (1991) carbonhydrates, more accurately hemicellulose and pectins account for 60%, lignin derived 30% and extractives approx. 10% of DSC. (Wågberg and Ödberg 1991;Hubbe et al. 2012).

Research on COD content of TMP process waters is scarce but in contrast Thornton (1993) has performed detailed studies on DCS content of TMP process waters. Table 3 represents a summary of COD content in TMP and DIP process waters. The COD values of TMP are calculated by weighting Thornton´s DSC values with theoretical COD and by using 75-90% scale (Lenes et al. 2001) as an assumption. The two major COD forming component groups in unbleached TMP process water are carbohydrates and lignin-like compounds (see table 3). This is stated also in the study of Jahren et al. 2002. Once TMP is bleached the process components in process waters change thus changing the relative proportion of the components that are measured as COD. A group of carbohydrates decompose forming low molecular weight acids (mainly acetic acid) (Thorton 1993). Respectly COD content comprises mainly of lignin-like material and low molecular weight acids.

Table 3 A summary of the COD content of TMP and DIP process waters

COD	TMP, unbleached (%)	TMP, bleached (%)	DIP (%)	References
Carbohydrates	30-40	15-20	20	Thornton 1993; Lenes et al. 2001 /RØring and Wackerberg, 1997
Ligninlike material	20-30	20-30	50	Thornton 1993; Lenes et al. 2001 /RØring and Wackerberg, 1997
Low molecular weight acids	<5	20-30	20	Thornton 1993; Lenes et al. 2001/RØring and Wackerberg, 1997
Extractives	15-20	10-15	6	Thornton 1993; Lenes et al. 2001/RØring and Wackerberg, 1997
Lignan	<10	<5	-	Thornton 1993; Lenes et al. 2001
Tot.	75-90%	75-90%		

3.1.2 DIP process waters

Chemical characterization of DIP white waters indicate that COD components fall in categories of lignin derived, carbohydrates, acetic acid and extractives. Lignin derived substances explain roughly 50% of the

COD found in DIP waters which is higher than in mechanical pulping white waters. Carbohydrates and acetic acid account for fewer than 20% and around 6 % for extractive according to Roring and Wackerberg (1997). In the study of Holmbom and Sundberg (2003) starch (carbohydrate) is stated as the major compound of DCS. Table 2 represents that lignin is stronger COD substance than carbohydrate (1.9 vs. 1.2) which denotes that depending on the rations of COD components dominating DCS can be carbohydrates but dominating COD compound lignin. Table 3 summarizes the COD content of DIP process waters.

3.1.3 Paper machine process waters

COD characterization of paper machine waste water and COD potentials of paper making chemicals are scarcely studied but composition of COD in these waters can be evaluated based on the knowledge on the COD composition of the pulps used in the paper making. Mechanical pulps are highly contaminated with DCS since usually only dewatering not effective washing is included into the process. Deinked pulps are cleaner since recycled paper is intensively washed in the process. DCS characterization in TMP and DIP pulps indicate that DCS releasing from DIP is starch (glucose units) and from TMP are especially glucomannans and pectins (carbohydrates). In newsprint production most of the released DCS is originated from mechanical pulp. Extractives (pitch) and lignans (mainly hydroxomatairesinol, HMR) are additionally typical releasing DCS when Norway spruce is used in newsprint production. (Holmbom and Sundberg 2003).

Similarity of COD compounds in TMP and DIP process water indicate that 5-component analysis suit well for characterization of COD in the paper mill studied in this thesis.

4 REMOVAL OF COD BY INTEGRATING KIDNEY SYSTEMS

This chapter introduces widely studied internal COD removal methods. Internal purification methods, i.e. “kidneys”, are interesting due to their potential to reduce water consumption if process water can be circulated. Methods for process water purification are numerous and all the strategies have their own removal efficiencies based on each contaminant thus combining two or more techniques brings synergistic benefits and better purification result. Best-known strategies for purification according to Concepción Monte et al. (2001) include techniques from membrane filtration, biological treatment in aerobic or anaerobic conditions, enzymatic treatments, oxidative treatments, and multiple effect evaporation (Concepción Monte et al. 2001).

Before considering any internal contamination removal strategies alternative approaches to reach appropriate process water quality should be considered at each mill. The first approach is to increase washing of the pulp before it enters to the paper machine since sufficient cleanliness can be reached by better washing. In this approach the much of the COD load is left at the pulp plant thus paper machine is kept cleaner. The second approach is the enhanced use of retention aids that compensate for effects of dissolved organic material, colloidal material and enriched salt ions present in white water. (Hubbe 2007b).

4.1 Dissolved air flotation (DAF)

Removal of contaminants with DAF is based on generating pressurized air solution into water. The air bubbles then attach to problematic components bringing them to the surface of flotation cell where they can be removed. DAF is one the most commonly used internal purification method due to the capability to treat large quantities of water and wide range of solids content. In principle reduction of suspended solids (e.g., fillers, fines, fibers, and ink particles) is efficient (up to 80-98%). Unfortunately, removal of DCS is limited: The reduction of DSC (measured in COD) with DAF is

only 10-30% since most of COD causing components are extremely small (under 0.2 µm). (Øpedal et al. 2011). Especially DCS contaminants in DIP waters proved to be difficult to remove by DAF I the study of Ben et al. (2003). They concluded that DAF with bentonite/polyacrylamide chemistry was found to be efficient in removal of large suspended solids but DCS removal rate was very low. Hence DAF fails in removal of many detrimental compounds in TMP and DIP process waters. Chemical optimization, for example with dual system (a cationic coagulant and a cationic flocculent is used together) is required to agglomerate thus retain colloidal compounds in deinking process. (Miranda et al. 2008)
In TMP process waters a combination of two polymers (Poly-DADMAC + C-PAM) produced removal efficiency of 75% for colloidal extractives in a study of Øpedal et al. (2011). This is probably due to a successful flocculation mechanism including charge neutralization and flocculation. Additionally, in the study of Miranda et al. (2009) DAF treatment with a pretreatment of whitewater by soluble aluminum compounds and high-charge cationic polyelectrolytes achieved 90 % removal of pitch compounds.

Performance of DAF can be enhanced also by involving a direct current to a pair of electrodes near to the flotation cell entrance (Hubbe 2007b). Basic concept is that metal ions dissolved from the anode attract small contaminants that flocculate into larger units. Cathode generates hydrogen bubbles that lift the colloidal and particulate material to the surface. (Partanen 2013).

DAF operates best in removal of dissolved solids but with optimal chemical additives added prior to the clarification unit removal of some colloidal particles (> 0.2 µm) is possible to achieve. However, as said earlier DSC smaller than 0.2 µm stays in process water thus requiring additional internal water treatment. This is emphasized in the study of Concepción Monte et al. (2011). Their results indicate that DAF efficiency for dissolved

COD and cationic demand in newspaper production process waters is completely inefficient.

4.2 Membrane filtration

Membrane filtration separates substances from liquid based on their size. Figure 2 represents sizes of various components in paper and pulp effluents in relation to a variety of filtration methods: Microfiltration can remove suspended solids and bacterial cells, ultrafiltration separates polysaccharides, extractives and high molecular mass lignous compounds, nanofiltration even multivalent salts and reverse osmosis can separate essentially everything except water including monovalent ions (e.g. corrosion causing chlorine). Basically the membrane pore size specifies the contaminant type that can be removed. (Nuortila-Jokinen 2004; Hubbe 2007b; Simstich and Oeller 2010).

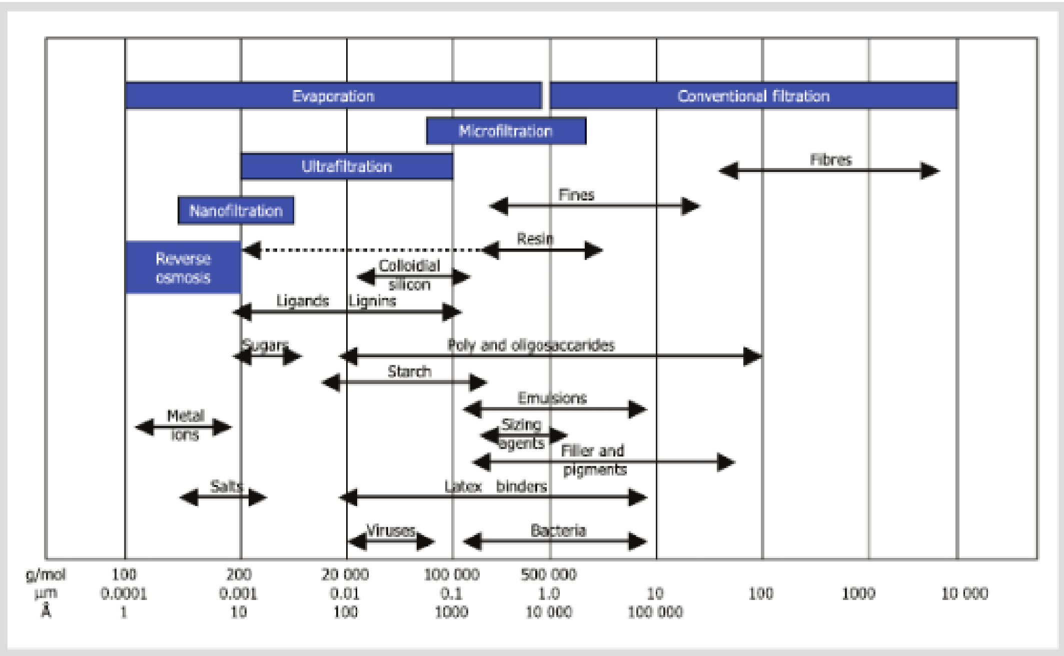

Figure 2 Sizes of various components in the waste waters of pulp and paper industry (European commission 2013)

Membrane techniques are recommended for white water purification (Hubbe 2007b;Nuortila-Jokinen et al. 2004) for their economical competence and versatile nature. Firstly, they can be applied to variety of processes, secondly, various points within the process and finally, they can remove organic *and* inorganic impurity loads. Ultrafiltration removes slime problems from paper machine and permeate can be used as paper machine shower water thus reducing water consumption. (Nuortila-jokinen et al. 2004). Ultrafiltration can accomplish 30% removal of organic load. With nanofiltration most of the organic contamination and multivalent ions such as calcium, iron, aluminium, silicon, magnesium and sulphate that can enrich in the process and cause deposits and corrosion are excluded. The nanofiltration permeate can be utilized instead of fresh water even in high pressure showers in paper machine. Figure 3 shows retentions for ultra- and nanofiltration of certain components typical for mechanical pulping waters. Retention of the organic material (TC) in nanofiltration is three times higher compared to ultrafiltration but arguing that *ultrafiltration, regardless of the larger pore size,* is most progressive for white water purification can be justified for two reasons. Firstly, flux is higher in ultrafiltration than in nanofiltration and secondly under 10 nm material, high-mass polymeric material and colloidal wood processing byproducts, that are found to interfere most with additives in wet end (e.g. cationic retention aid) can be removed with ultrafiltration pore size. (Hubbe 2007b).

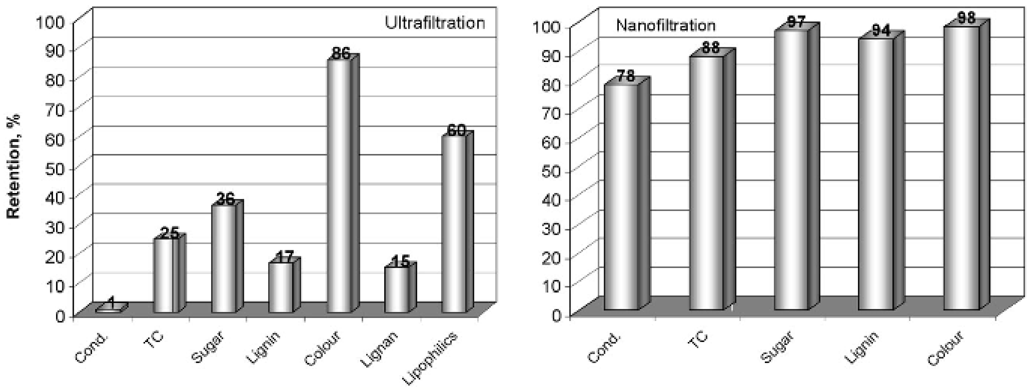

Figure 3 Retention of components from groundwood mill circulation waters (Nuortila-Jokinen et al. 2004)

Ultrafiltration is a sufficient internal treatment to reduce COD loads in many cases but when aiming for drastic water reductions and system closure ultrafiltration alone cannot produce required water quality since dissolved substances, such as organic polymers or dissolved salts aren´t retained.(Simstich and Oeller 2010). Even though ultrafiltration is regularly used in pulp and paper industry suitability for every process must evaluated case by case. For example, the study of Concepción Monte et al. (2011) shows that the removal efficiency of ultrafiltration for dissolved COD (DCOD) and cationic demand (CD) in newsprint production is only 20% for DCOD and 10% for CD. On the contrary the results in LWC production are 60% for DCOD and 80% for CD. This highlights the importance of knowing the water quality and tracing the components before installing any treatments methods.

For mechanical pulping process conditions ceramic membranes can deliver efficient result. Ceramic nanomembranes tolerate high temperature hence ultraclean permeate is produced while keeping thermal energy within the process. Higher investment cost are compensated by better energy balance, longer service life and higher flux compared to some synthetic polymer membranes that fail in TMP process temperatures. (Hubbe 2007b;Simstich and Oeller 2010.).

Major limitations for wider use of membrane techniques in pulp and paper industries results from low flux capacity and membrane fouling as a consequence of the similar size of pore size and contaminants (Hubbe 2007b;Nuortila-Jokinen et al. 2004) hence there is frequently a compromise between throughput of water, fouling resistivity and separation capacity. Measures to overcome limitative factors have been developed and membrane systems can be enhanced by pre-treatment to produce higher permeate flows and to defeat membrane fouling. (Hubbe 2007b). Pre-treatment methods are plenty, e.g., chemical treatment, biological treatment, and ozonation but according to Nuortila-Jokinen et al. (2004) the most cost-efficient pre-treatment methods in the case of mechanical pulping plant waters are chemical flocculation, pH adjustment and thermophilic aerobic biological treatment. (Nuortila-Jokinen et al. 2004).

4.3 Chemical coagulation

Coagulation neutralizes particles causing suspended materials to agglomerate into larger units thus serving a pretreatment method for other kidneys. In general three flocculation strategies are implemented in pulp and paper mills: i) a single cationic flocculent with a low to a medium cationic charge and very high molecular weight (e.g. PAM), ii) a coagulant with high cationic charge and low molecular mass (e.g., poly-DADMAC) and high molecular weight anionic flocculent (e.g., A-PAM) used together, iii) a dual system where a cationic coagulant and cationic flocculent are used together. (Miranda et al. 2008). In a study of Nurmi et al. (2006) the best performance for mechanical pulping waters was obtained at a medium to high level cationic charge (C-PAM with a molar mass of 9 · 106 g/mol and a charge density of 3.2 meq/g). C-PAM affected most on extractives, triglyserides and steryl esters. (Nurmi et al. 2006)

An innovative approach producing agglomerates in an aqueous solution is coagulation with direct or alternating current. Electrochemical activation has been incorporated to a paper mill effluent clarifier treatment at Niederauer Mühle. (Hubbe 2007b).

Most simple approach of the coagulation within paper machine operations might be just to add the coagulant to the stock system and the high-mass copolymer just prior the forming sections thus including the fine material in the product and away from the water. (Hubbe 2007b).
Flocculation is a useful pretreatment for, for example, flotation and ultrafiltration but by itself does not deliver efficient purification. (Hubbe 2007b).

4.4 Biological treatment

Biological treatment is usually applied subsequent to papermaking but, usually, at least one stage of biological treatment is applied when attempting water system closure which is the ultimate level of water consumption reduction. Biological treatment is alone insufficient for total closure of water cycle thus other treatment, such as membrane technologies or evaporation is required. (Allender et al. 2010). Especially, within recycled paper based mills biological treatment has significant benefits since in addition to relatively efficient removal of COD elimination of bacteria is achieved (Huhtamäki 2003). Jahren et al. 1999a evaluated the suitability of biological treatment methods (aerobic moving bed bioreactor, MBBR) and anaerobic hybrid reactor which consists of an upflow anaerobic sludge blanket reactor (UASB) and a filter as a strategy in TMP mill closure. In their study anaerobic hybrid reactor was preferred to be combined with another treatment, such as nanofiltration, when building a feasible strategy for closing the water circuit in TMP process. (Jahren et al. 1999a). Aerobic MBBR has performed well in the study of Widsten et al. (2004) where bio-kidney performed 71-92% removal efficiency for COD in TMP white waters. Biological treatment is efficient in removing carbohydrates and lignan since TMP white waters consists mainly from carbohydrates biological methods are reasonably feasible. The removal efficiency of COD for lipophilic extractives and lignin-like components is low, in aerobic MBBR only 25-35% and in anaerobic hybrid reactor only 16 %. (Widsten et al. 2004;Jahren et al. 1999b).

Anaerobic treatment is an intriguing possibility to produce energy via methane production in addition to contaminant removal. Other advantages over aerobic treatment are lower sludge production and lower energy consumption. (Barascud et al. 1992). Anaerobic reactor has performed well in COD removal but aerobic treatment has its benefits too. Well aerated process water helps to avoid anaerobic conditions in paper machine which is linked with fouling, odors and corrosion (Geistbeck

1994). Habets & Knelissen (1997) and Alexandersson & Malmqvist (2005) studied the removal of COD by combining anaerobic and aerobic treatment with white waters of packaging paper mill. During first stage dissolved organic compounds (such as carbohydrates and volatile fatty acids) are converted into methane and sulphate reducing bacteria convert sulphate into hydrogen sulphide which is then stripped out by the biogas. In the aerobic part residual organic components are oxidized into carbonate which precipitates with calcium ions into the aerobic sludge and then accumulates as calcium carbonate. The treatment achieved high removal of soluble organic material (87%) in varying loading levels but accommodating accurate nutrient dosing accordingly was experienced as a difficult task due to the complex matrix of whitewater. Optimal nutrient dosage is vital to the final quality of processed water since lack of nutrients is a limiting factor thus key in removal efficiency. On the other hand, excess nutrients create slime growth and may decrease runnability on paper machine which results in enhanced use of biocides and retention aids. (Habets & Knelissen 1997;Alexandersson and Malmqvist 2005).

The Benefits of combining anaerobic and aerobic are high COD removal, tackling the buildup of volatile fatty acids, substantial reduction of sulphate and even in some cases digesting of wood resins (Hubbe 2007b).
Thermophilic conditions in biological treatment are more preferable in TMP process in terms of energy balance since operating in process temperature reduces costs when additional cooling and heating of treated process water is unnecessary. In the case of anaerobic biological treatment the yield of methane is also higher in thermophilic conditions vs. mesophilic. (Jahren et al. 1999b). This should be considered when choosing biological treatment to TMP process.

4.5 Enzymatic treatment

Use of scavengers and improved washing has been traditionally an approach to control DSC in paper making but some researchers (Linhart et al. 1989; Sjöström et al 2006; Ni et al. 2011) propose that focusing attention on individual components in DCS would evolve their control. Enzymatic strategies are based on enzymes´ ability to degrade specific groups of components hence potential enzymes can be selected to break down or modify a certain compound group of DCS present in process waters. Thus enzymatic treatment could be a solution to control the effects of DSC. (Hubbe et al. 2012).

Enzymes are produced by living natural sources, for example, bacteria or fungi. Using enzymes rather than living cells greater selectivity and control can be accomplished, quicker reaction times and greater tolerance for high temperature is achieved (Hubbe 2007b;Widsten and Kandelbauer 2008;Zhang et al. 2002). Degradation of specific process water contaminants can be achieved by using enzymes: Laccase has demonstrated a great potential to reduce wood extractive problems in TMP and newspaper mills according to Zhang et al. (2005). In TMP white waters lipophilic extractives were reduced by up to 25% and hydrophilic extractives by over 60%. In paper machine white water reductions were respectively 50% for lipophilic extractives and 90% for hydrophilic extractives. (Zhang et al 2005). Zhang et al. (2002) studied removal of DCS from TMP/newsprint mill white water by a combined fungal and enzyme treatment. Specific enzymes degrade certain DCS, for example, lipase and laccase solve pitch problems but to deal with the variety of DCS components a range of enzymes is required. In their research three enzymes (laccase, lipase and cellulose) and white rot fungus, T.versicolor, was studied. Fungal culture filtrate degraded significant amounts of many DCS compounds when injected directly to white water circuit: Over 90% of lignans and ester bonded extractives (steryl esters and triglycerides) was removed (after 3h, 65°C), 40% removal of resin acids, 60% removal of fatty acids and 62-71% of removal of carbohydrates (after 7 days) was achieved. In contrast lignin content increased probably due polymerization during fungal treatment. In the study of Widsten et al. (2004) the COD values actually increased after laccase treatment due to the biomass of the enzyme itself. (Widsten et al. 2004;Hubbe 2007b).

Enzymatic oxidation results in high removal efficiency of DCS including some calcitrant components hence research show that enzymes can be used to alleviate the problems derived from wood-based white water contaminants. Interestingly, enzymatic treatment may increase COD values thus other treatment might be obligatory to reach COD limitations. Enzymatic treatment might be feasible as a pretreatment to degrade some component, e.g., hemicellulostic macromolecules, thus preventing the formation of strong complexes between hemicellulose and cationic additives or dealing with calcitrant extractives. (Widsten and Kandelbauer 2008, Pokhrel and Viraraghavan 2004, Zhang et al. 2005).

4.6 Oxidative treatments

Oxidation is an interesting technique to degrade calcitrant components (including organohalogens, dyes, pesticides and surfactants) present in white waters (Agustina et al. 2005) since organic compounds thermodymically unstable to the oxidation are *actually eliminated* not just transferred from one phase to another (Molina 2002).

Advanced oxidation processes are based on formation of hydroxyl radicals (•HO) that later oxidize organic compounds. Oxidation with hydroxyl radicals is a chain reaction where hydroxyl radical abstracts hydrogen from organic molecule thus generating organic radical and water. Reactions proceed forming hydroperoxide that in final reactions 1) reacts with organic compounds to yield alcohol or 2) decomposes into ketones and eventually acids. Decomposition reactions continue and low weight acids will be finally converted into carbon dioxide and water. (Molina 2002).

Hydrogen radicals can be generated by various means: by UV-radiation, ozonation, Fenton process and wet oxidation. In UV-radiation processes, for example, hydrogen peroxide and TiO_2 is often utilized. Fenton processe is an advanced oxidation boosted with an iron catalyst: hydroxyl radicals are generated by decomposition of H_2O_2 catalyzed by iron salts. (Nesheiwat and Swanson 2000). Wet oxidation is flameless radical oxidation where contaminants containing liquid is mixed with gaseous source of oxygen in high temperature and pressure. High temperature and pressure increase the costs of this efficient method thus a compromise between the costs and contaminant removal is evident in practice. (Molina 2002; Levec 1997). Table 4 represents Results of COD reduction in lab-trials using the membrane concentrates. Table 4 represents also the capacity of ozonation, wet and Fenton oxidation to crack the compounds into biodegradable form.

Table 4 COD reduction efficiencies of ozonation, wet and Fenton oxidation (Nuortila-Jokinen et al. 2004)

Trial	Direct COD elimination	Aerobic degradation	Anaerobic degradation	Comparative costs
Concentrate without treatment	0%	0–5%	0–5%	–
Ozone	25–45%	25–35%	5–15%	Medium
Wet oxidation UV/H_2O_2	20–40%	15–50%	5–15%	Medium–low
Fenton oxidation	20–60%	25–50%	5–40%	Medium–high
Electro chemical	10–30%	0–10%	0–5%	High
Flocculation/precipitation	25–50%	0–5%	0–5%	Medium–low

Agustina et al. (2005) concluded that some recalcitrant organic compounds are difficult to remove by ozonation or photolysis alone and they can even convert the compounds into dangerous forms but with a combination of several treatment methods, such as, O_3/VUV (ozone,vacuum ultraviolet), O_3/H_2O_2/UV (ozone, hydrogen peroxide,ultraviolet) and UV/H_2O_2 (ultraviolet,hydrogen peroxide) improved removal of contamination is achieved (see figure 4).

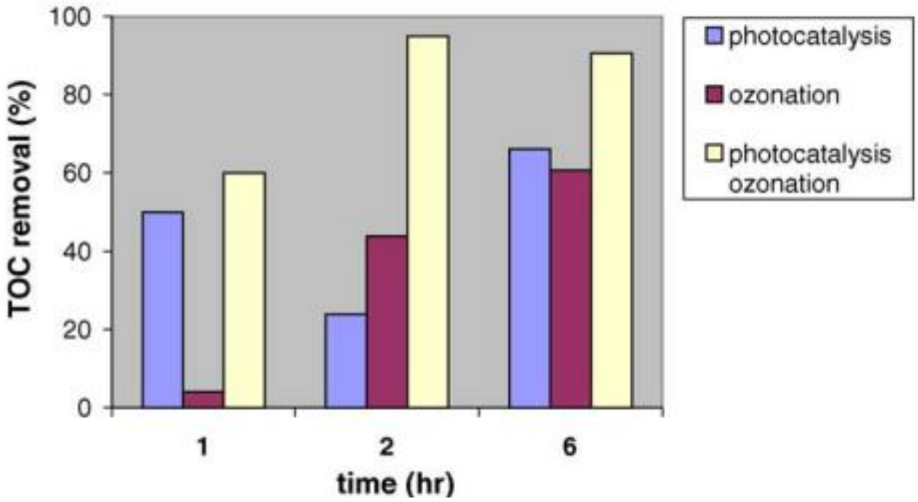

Figure 4 Degradation of various organic compounds (textile effluent) by using photocatalysis, ozonation and their combination. Agustina et al. (2005)

Kopf et al. (2000) calculated the energy consumption per dissolved organic carbon (kWh/g DOC reduction) of three methods. Photocatalysis TiO_2/O_2, ozonation H_2O_2/O_3 and photocatalytic ozonation TiO_2/O_3) are represented in table 5.

Table 5 Energy consumption per dissolved organic carbon of three oxidative methods (Kopf et al. 2000)

	TiO_2/ O_2 (kW h/g DOC-reduction)	H_2O/O_3 (kW h/g DOC-reduction)	TiO_2/O_3 (kW h/g DOC-reduction)
Monochloroacetic acid	19	110	5.4
Pyridine	120	73	11

Photocatalytic ozonation resulted much lower specific energy consumption compared the two other methods.

4.7 Evaporation

Evaporation is based on separation provided by heat. Heat increases the liquid temperature to the boiling point which removes most of the dissolvent leaving a concentrated solution as a result. Water free from salts and most organic matter, with possible exception of some low boiling organic material (low-mass alcohols, acetic acid, volatile fatty acids etc.), is generated when vaporized water is condensed. (Bourgogne and Laine 2001). Evaporation is an effective treatment for pulp and paper process waters achieving up to 97% of COD and TOC reductions (Gartz 1996). Paper mill waste heat can be utilized in the approach of closing the paper mill water cycle and evaporation has been considered to be a future treatment method in a field of pulp and paper water processing (Molina 2002). BREF-documents state that especially multi-effect vacuum evaporation are promising for mechanical pulp and paper mills since sufficient amounts of waste heat is available to operate the treatment system. (European Commission 2013)

Evaporation generates high quality water. Most of the evaporated water is clean condensate which can be used in pulp production. COD of clean condensate in CTMP plants could approximately be < 500 mg/l and in TMP plants even < 150 mg/l. (Pöyry unbublished 2013) .
The drawbacks of evaporation are large space requirement and high consumption of energy since the effluent concentrations are low in pulp and paper production which results in high costs (Molina 2002). Technical advances have lowered scaling and corrosion tendency and reduced costs associated with the technique (Bourgogne and Laine 2001). Consequently, evaporation is most recommended for treatment of relatively small but highly contaminated water (Hubbe 2007b).

Evaporation is highly efficient in contamination removal from process waters but attendance to the *concentrates* of evaporation is required. Laari et al. (1999) studied the treatment of evaporation and membrane concentrates by ozonation and catalytic low pressure-wet oxidation. They found that catalytic low pressure-wet oxidation (under 150 celsius) achieved 50% COD reduction following by increase in biodegradability. Ozonation as a concentrate treatment in TMP process proved to be economically problematic since removing of lipophilic extractives required high ozone dosing. (Laari et al. 1999)

Costs of evaporation can be reduced by installing only pre-evaporation which aims for smaller solid content. Alternative for pre-evaporation could be a multi-effect evaporation plant (MEEP) comprising a series of several evaporation units and a mechanical vapour recompression (MVR) evaporation plant. Costs remain relatively low compared to other evaporation techniques since MEEP evaporation is mainly aided by steam hence electrical demand is decreased. (Pöyry unbublished).

4.8 Combinations of purification methods

Paper mills aiming to water cycle closure or highly reduced water consumption benefit from the synergist effects combining separate treatment methods can offer. Nuotila-Jokinen et al. (2004) recommend chemical flocculation and thermophilic aerobic treatment followed by nanofiltration to be most cost-effective in *mechanical pulping and paper mill* process waters. The simplest approach would be taking benefit from external waste water treatment plant by circulating active sludge plant discharge via membrane filtration and then back at the mill. (Nuotila-Jokinen et al. 2004). In addition pretreating white water with high charge cationic fixatives prior to membrane filtration is recommendable to hinder membrane fouling thus losses in flux Hubbe 2007a). Tardif and Hall (1997) reported some 70% removal of dissolved COD in Membrane bioreactor (MBR). Also Simstich and Oeller (2010) pointed out in their research that combining of biological and membrane techniques is the future method in continued water savings. As earlier represented, combination of biological methods have proved to be effective in treatment of TMP process waters.

Tardif and Hall (1997) reported 63-76% removal of dissolved COD in sequencing batch reactor (SBR). Furthermore, MBR and SBR removed extremely effectively resin acids (up to 100%) and fatty acids (84% and 76%).

In the treatment of waste paper process waters a combination of anaerobic and aerobic treatment achieved 88-93% reduction in COD (Alexandersson et al. 2005). Kabdash et al. (1996) reported a combination of chemical and biological treatment, i.e. bioferric method, to remove additional 40-50% of COD compared to activate sludge system.

Other interesting and effective treatment combination is a combination of coagulation and wet oxidation. In the research of Verenich et al. (2001) 51% COD reduction and 75% reduction of lignin was achieved. Efficient lignin degradation was reported in kraft pulp process water treatment with a combination of ozone and activated sludge process (Nakamura et al. 1997).

Appendix 1 represents a summary of the treatment methods described earlier in the chapter 4.

Selecting a treatment method is highly dependable on the investment costs and the use of costs. Table 6 represents some water treatment possibilities and their investment and operational costs.

Table 6 Water treatment possibilities and their investment and operational costs European Commission 2013, p.216)

Water treatment methods	**Electricity consumption kWh/m³ water**	**Typical capacity (m3/d)**	**Investment costs Euro/(m³/d)**	**Operational costs Euro/(1000 m³)**
Chemical treatment of raw water	0.30	30000	170	73
Biological effluent treatment	1.20	30000	620	136
Microflotation	0.23	10400	20	104
Ultrafiltration	2.60	5000	470	153
Multiple effect evaporation	1.34	3600	840	35
Mechanical vapour compression	13	3600	1360	328
Cooling tower	0.12	39000	130	3
Note: Figures are based on equipment deliveries only and total project costs/local application costs are not included				

5 CONTROL OF COD

5.1 Control by washing and retention

Before considering any treatment methods enhanced use of retention aids or washing of pulp could be eligible means compensating the negative effects of colloidal and dissolved components and enriched salts etc. (Hubbe 2007a) at the paper machine.

5.1.1 Retention

Retention is an interesting phenomenon since binding DCS onto fibers decreases naturally the DCS content in waters. Retention of colloidal fines has been effective by two stage retention aid treatment containing neutralizing at least part of surface charges and secondly binding fiber fines and other material onto cellulostic fibres with a very high mass flocculent. (Hubbe 2007a). However, possible decrease of paper strength and brightness may restrict the use of the strategy.
In the attempt to bind colloidal material to larger cellulostic material (and hence to be removed with the end product, paper) fixing agents or so called scavengers are utilized. (Hubbe 2007b). Scavengers are inexpensive material, such as, talc or hydrophilic organic polymers (e.g. polyvinylalcohol) that cover the sticky layer of the compound rendering them less deportable (=pitch and stickies control). Also Poly-DADMAC, polyethyleneimine (PEI) and polydemethylamine- epichlorohydrin (PAE) are commonly used in pulping to control the negative impacts of detrimental compounds, such as stickies and anionic trash, in paper making. (Hubbe et al. 2012). Interestingly, also mannans can provide the effect of at least partly neutralizing DCS thus being to some extent a beneficial DCS compound (Holmbom and Sundberg 2003).

Next generation scavengers according to Hubbe et al. (2012) could be starch-based cationic polymers due to their biodegradability, renewability and cost-efficiency. Additionally, highly substituted cationic starch (HS-CS) causes aggregation and deposition of DCS on pulp fiber surface. The performance of dual-component-retention is probably due to charge neutralization system. (Hubbe 2012; Zhang et al. 2007 and 2009)

The content of process water is important when scavengers are exploited in water treatment since scavenger efficiency depends on the DCS compound. Sundberg et al. (1994) studied scavenging of DCS with high-charge, low molecular mass poly diallyl-dimethyl-ammonium chloride (poly-DADMAC) in unbleached and peroxide bleached TMP suspensions. They found optimum polymer dose (OPD) where destabilization of colloidal substances was at its highest for both suspensions to be for bleached TMP nearly twice the dose compared to unbleached TMP suspensions. DCS compounds interacted differently with the polymer: lipophilic extractives were almost completely destabilized by the polymer, anionic hemicelluloses interacted and neutral hemicelluloses affected only slightly with the polymer hence lipophilic extractives and dissolved anionic hemicelluloses formed aggregates with poly-DADMAC. (Sundberg et al. 1994).
Also Tanase et al. (2010) reported in their study that cationic polymers can be used to precipitate hydrophobic DCS compounds but removal efficiency was highly depended on the DCS component and wood species.(Tanase et al 2010)

Other possibility to scavenge DCS is to pre-absorb very high-charge cationic agent onto fine solid material, such as, silica particles which then adsorb and retain DCS material in paper sheet (Guyard et al. 2006). Guyard et al. (2006) found high-charge cationic polymer modified by silica particles to be efficient in adsorbing polygalacturonic acid (a building blog for anionic trash) and retaining the precipitated matter in paper sheet. Also zeolites have been studied due to their adsorptive nature. Bourassa et al. (2003) reported nanoporous structure of zeolites adsorbing effectively large amounts of trash, such as, calcium and manganese ions which are connected to pitch deposits and scale formation. (Bourassa et al. 2003;Hubbe 2007a)

Feasibility of retention of DCS thus COD need to be evaluated case by case. Traugott and Berger (1989) modeled the two alternatives: i) fixing the detrimental components in the paper and ii) discharging them with highly loaded waste water. Based on costs and feasibility they favored the latter. (Traugott & Berger 1989). Even though changing the COD problem into paper bulk sounds tempting the chemical costs and possible problems due to contaminated pulp in paper machine limit the usage of the method.

5.1.2 Washing

Washing of pulps serves two benefits: Firstly, cleaner pulp enhances the process conditions and secondly removing the contaminant early in pulp plants enables selective removal of the load.

The priority of washing is to remove dissolved organic and inorganic material that would otherwise contaminate pulp and complicate subsequent sequences (Sillanpää et al. 2001). Minimum amount of contaminants should pass over to the wet end thus segregation is needed. Carry-over can be decreased significantly when counter current water system is introduced: Fresh water is used at the paper machine and excess water is taken out from the pulp mill side. This is combined with pressing the pulp to a high consistency and keeping the dewatering waters in pulp mill cycles. (Holmbom and Sundberg 2003).

Improved washing of pulps before paper machine ought to be considered to prevent contamination migration. Eliminating contamination from furnish early in the process enables reductions in the water treatment costs. (Huhtamäki 2003; Hubbe 2007a). In mechanical pulping and recycling of waste fibers improved washing before paper machine has a potential to enhance the paper quality and reduce costs associated with wet-end chemicals (Hubbe 2007a). The role of washing is amplified in the mills of reduced water consumption. Especially, intensified washing during bleaching of kraft pulp has significantly lowered the effluent discharges from bleaching (Sillanpää et al. 2001). In addition, optimized washing decreases the chemical need.

Käyhkö (2002) reported in his thesis that wood resin content in mechanical pulp can be significantly decreased if the process contains peroxide bleaching and subsequent washing stage. With optimal process configuration up to 85% of deresination can be achieved (Käyhkö 2002).

Sillanpää et al. (2001) describe better washing practices in kraft pulping in their article. They conclude that fractional washing where the filtrates are divided into two or three fractions according to their chemical properties improve the washing results. Especially, benefits are gained in removal of quick leaching components, such as metal ions and small ions. (Sillanpää et al. 2001)

Improved washing enhances the control of COD in paper mill by achieving flows with highly concentrated COD loads but additional methods need to be applied to remove the loads before the final end, water courses.

5.2 Chemical control

5.2.1 TMP

Alkalinity strongly effects on the dissolution of hemicelluloses and pectins thus other alkali sources that operate in lower pH has been proposed. According to Suess et al. (2002) pH buffering effect of $Mg(OH)_2$ can be exploited. Peroxide bleaching with $Mg(OH)_2$ instead of NaOH leads to decrease in generation of dissolved organic compounds and consequently 30% to 40% reduction in the COD load (Suess et al. 2002). $Mg(OH)_2$ -based peroxide bleaching operates initially around pH 9 while in NaOH-based the pH is approximately 11-11.5. Respectively, the final pH values are approx. 7.5 for $Mg(OH)_2$ and approx. 7.5-9 for NaOH bleaching. Peroxide bleaching with $Mg(OH)_2$ not only replaces NaOH but also most of the silicate. In addition to lower COD loads magnesium based bleaching generates less anionic trash and stabilizing agents are required less due to more stable bleaching conditions. In addition opacity and dewatering improve, calcium scale formation is inhibited and even pulp yield is improved. (Ye et al. 2012; Harrison et al. 2008). On the other hand longer reaction time is required due to lower pH. Solubility of $Mg(OH)_2$ is poor thus intense mixing is required to prevent sedimentation. In addition, brightness and tensile strength decreased in the study of Ye et al (2012) when partial substitution of NaOH with MgO was studied. (Ye et al 2012).

5.2.2 DIP

Laboratory and mill scale experiments on reduced alkaline deinking incorporating sodium sulphite (Na_2SO_3) has been explored. Approach where sodium sulphite replaces or reduces sodium hydroxide, hydrogen peroxide and silicate decreases the COD load in recycled fiber plant (RCF). Kemira has performed several full scale trials in China and at least 20% COD reduction with similar or better ink release and floatation efficiency have been achieved compared to traditional method. (Wen 2011). Transition from alkaline deinking to reduced alkaline processing (in approx. pH 8) reduces also the anionic trash load, improves the control of pressure sensitive adhesive contaminants, reduces stickies aggravation and has a potential to decrease chemical costs (for example reducing DAF clarifier and sludge dewatering polymer usage). Research has concluded various results when operating with reduced alkaline pulp those ranging from equal bleaching response to lower results than in traditional bleaching. (Rosencrance 2007).

Patented non-sulphite neutral deinking is used in deinking mills. Method of eliminating peroxide, sodium silicate, sodium hydroxide, chelant and sulfuric acid causes pH to drop to 7-7.2 in the pulper which results as more stable process conditions. Studies regarding pulp brightness vary from the same to one point lower than with alkaline chemistry but post-bleaching eliminates the difference. With neutral de-inking pilot paper machine quality, runnability and cleanliness were the same or better and no deposit on paper machine felts or wires were observed. In addition the mill significantly reduced the polymer usage in DAF and sludge dewatering. (Rosencrance 2007).

EXPERIMENTAL PART

The experimental part comprises of two goals. The first is to create a reliable COD balance and the second is to subject the *modeling procedure* to investigation. The transparency of COD-modeling and reviewing the process is important to improve the model accuracy and the efficiency of the modeler. The models are represented in appendix 3 and 4.

6 MATERIALS AND METHODS

6.1 Data acquisition and modeling

Modeling starts with an extensive data acquisition from process, process equipment properties and process control philosophy in order to create a model equivalent to the real mill. The complexity of the model determines the water analyses and the amount of sampling points needed for modeling. In this work only one parameter was modeled in addition to water and mass balance hence only analyze of dissolved COD in various points was required. In addition to DCOD measuring research on process specific COD (COD formation in bleaching, in refining etc.) Information is required. In this case the water quality was studied along the modeling consequently other water analyses, such as, manganese, pH was measured.

Form, such as table 7, with clear columns of required information is a favorable means to obtain all the data first hand. Formula has advantages due to its unambiguous summarizing nature, common language and clear presenting. Water data is then readily available which enables the efficient use of data in modeling phase. This might seem overly simple but estimating and iterating of missing information or searching the scattered information is a major resource consumer.

Production data is vital to obtain *from the day sampling takes place* in order to connect the COD (or other components) at right level. In addition the process control system views are required from the day of sampling taking. The process control system views especially if the program is reasonably new bring valuable process information, such as, flow rates and consistencies. The information gained from the views can be used to evaluate model accuracy or estimate process flow rates.

Table 7 Example of information gathering. The formula contains the sampling points, their numbers, water analyses and process data.

	#ID		Analyses									Process data	
		average	CODCr (mg/l)	Dissolved COD (mg/l)	TOC (mg/l)	BOD (mg/l)	Conductivity (S/m)	pH	Temperature	SS (mg/l)	Manganese (mg/l)	Sampling date and time	PRODUCTION (ADT/d)
TMP	*1*	Filtrate from schip wash dewatering screw											
	2	Pressate from plug screw											
	3	Filtrate from reject press A											
	4	Clear filtrate from TMP disc filter											
	5	Cloudy filtrate from TMP disc filter											
	6	Clear filtrate from PM1											
	7	TMP disc filter feed											
	8	TMP heat recovery foul condensate											

The most time consuming part in modeling is to construct the architecture and layout equivalent to the actual mill. Flow sheets offer an appropriate base for process architecture but since those include all the connection variations (such as, those required only in start-ups) the process control philosophy has to be checked with the mill personnel. Time must be reserved for a proper examination of the flow sheets and close attention is required on equipment data (such as, efficiency, capacity, power data, etc.). In addition to the correct layout also the flow rates are in great role when high accuracy is targeted. This cannot be highlighted enough: water flows, especially between departments must be investigated as early as possible. The water flow rates should be most preferably investigated at the level of sampling day production since production effects on process water flow rates. This is important due to the operating feature of WinGEMS (the simulation software is represented in following section): Input water flows cannot just be altered “by one click”. Optimizing work is required to recover the balance in the model after any changes performed. Alterations are inevitable during the process but thinking ahead saves great amount of time since WinGEMS is not the most forgiving program.

Occasionally flow rate data can be difficult to access since many old mills do not have flow meters. This can be a problem since the model functions only at the accuracy level the given data has been provided. Model should be as equivalent as possible to the real situation; only equivalent model parameters will produce accurate results. Interviewing of mill personnel is required in order to determine equipment efficiencies and capacities, current operating practices, power data etc. In addition research on department specific COD is a must.

In this work simulations were performed by Metso WinGEMS 5.3. WinGEMS is a process simulator most widely used in the pulp and paper industry. WinGEMS contains a process block library and even whole pre-build process unit simulation blocks that can be integrated in any simulation. Every block is designed to run also without user modification.(Metso 2013). In this work the blocks were modified and many blocks were designed and built from scratch by “compound block” –tool.

6.2 Modeling of COD with WinGEMS

Working with WinGEMS starts with drawing the plant layout block by block (see figure 5) and stream by stream or alternatively by checking computations, stream components and balance calculations when using a ready base.

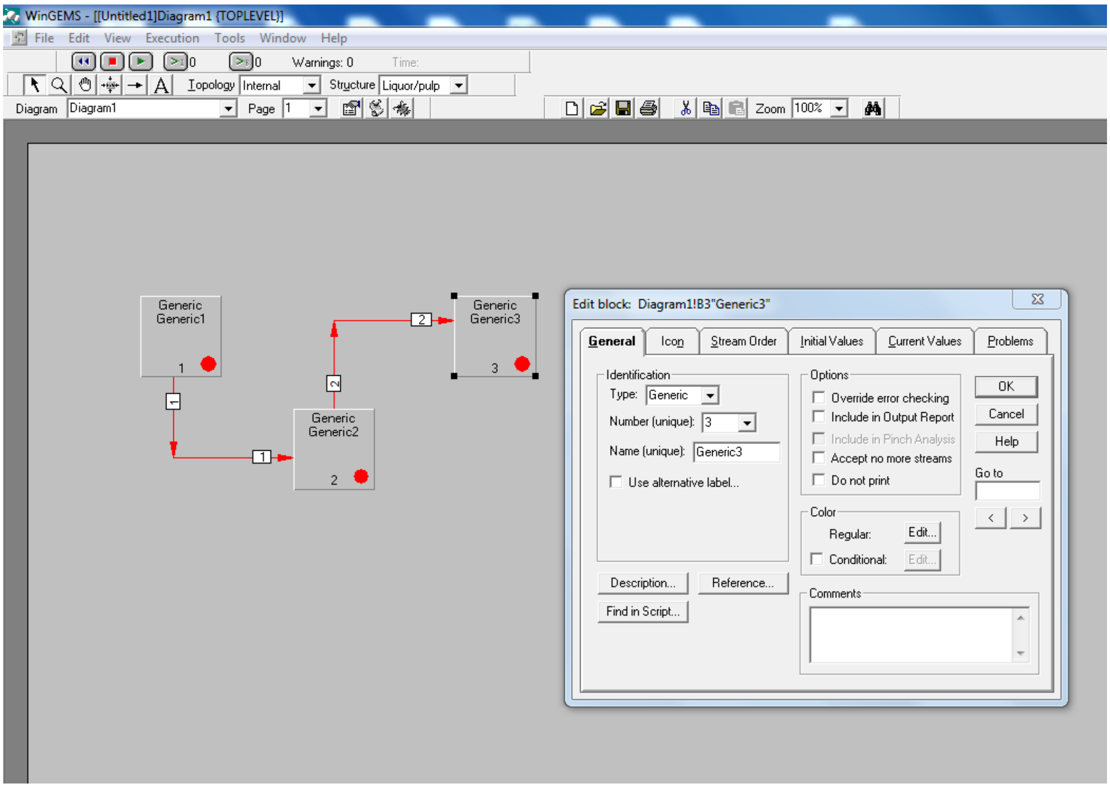

Figure 5 Building a model block by block and stream by stream with WinGEMS

Stream connections and equipment are added or altered according to the actual mill layout (see figure 6).

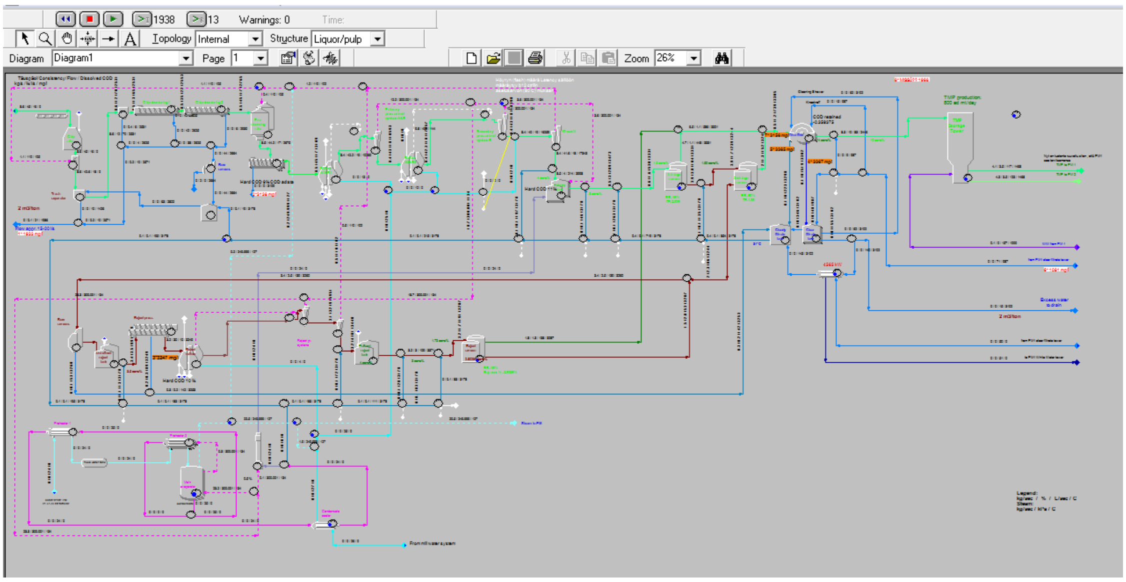

Figure 6 Complete architecture and layout

When the model layout is equivalent with the real situation, “controller” blocks are then used to direct requisite amount of water and mass to right places. Figure 7 represents the chip flow controller: Chip flow is determined by two parameters (1) monitored parameter: S581 which is the end product, TMP flow and 2) set point which is the amount paper machine requires TMP. The program then feeds increasingly chips as long as monitored parameter reaches the set point.

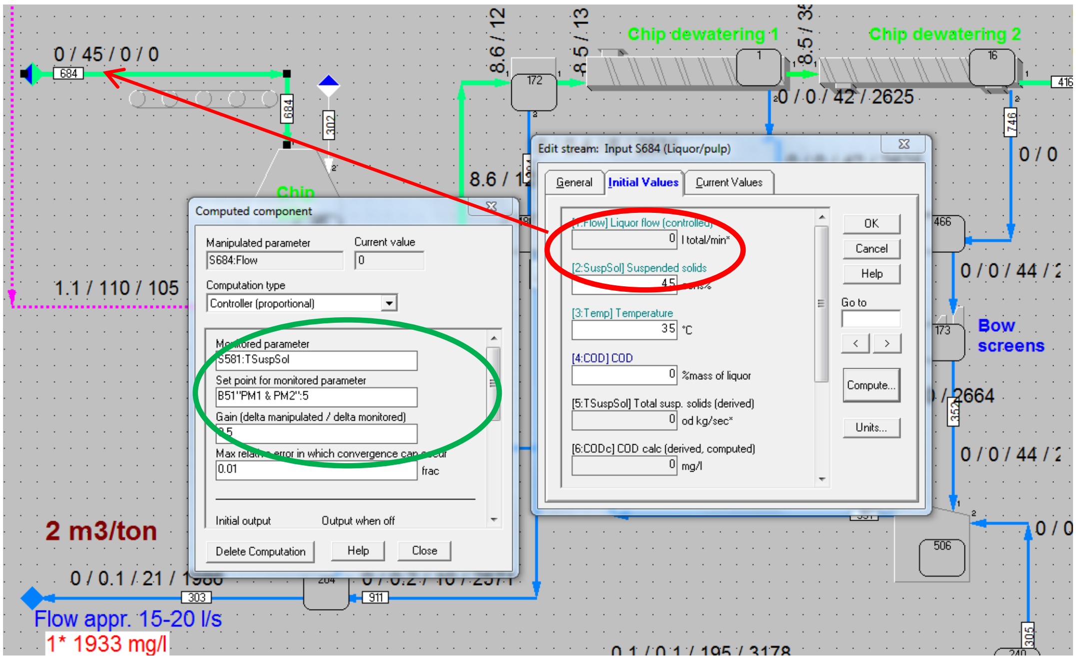

Figure 7 Simulation work starts: Controller setting. Controllers are like brains; they calculate and control the flows in the model.

Models contain dozens of controllers with varying duties. Dilution blogs are typical blocks that contain controllers (see figure 8). Those can be used to direct water to dilute pulp streams. Flows are usually preferred to be controlled in relation to production. Fixed values are naturally possible but controllers increase automation. In addition flow rate data is frequently lacking which leads to the fact that simulator must simulate the flow. This is done with controllers.

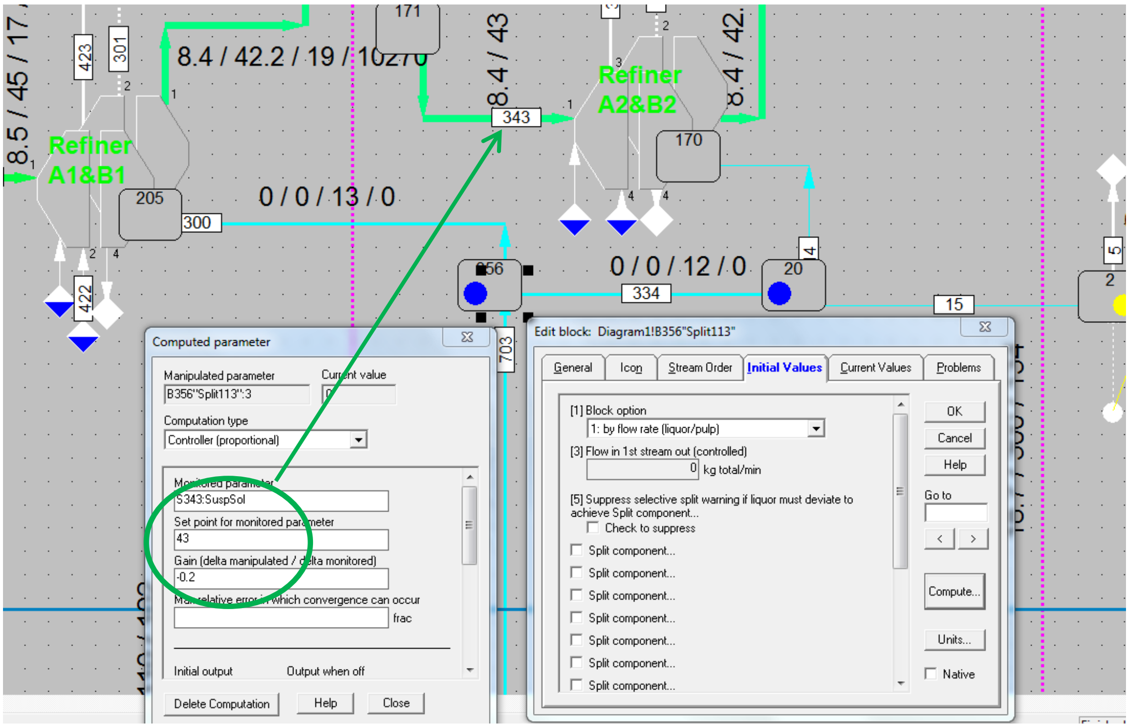

Figure 8 Dilution block sends water to refiner as long as the set point of (consistency 43%) is fulfilled. Here dilution block contains a controller that commands: "sent requisite amount of fresh water in order to reach 43% consistency in stream 343"

6.3 Adding COD in the model

COD modeling starts with process, department and raw material specific data acquisition. Modeler should possess a clear understanding on how COD behaves and migrates in the process, how COD is divided in equipment (pulp flow/filtrate), which equipment increase the COD load and how much. Unfortunately, this can be problematic since COD is rarely studied in the level of process streams and equipment data cannot be generalized. In addition not much of attention on specific process water parameters (besides of physical parameters, such as consistency and temperature) is traditionally paid. Against to this background it is evident that certain amount of process water analysis is mandatory in order to construct a reliable COD balance.

Seven sampling points was used to construct TMP and only 3 to construct PM model in this thesis. Approximately 15 is the minimum of sampling points in TMP and PM to create a reliable model.

The COD models in this work were constructed by using dissolved COD (DCOD). When using dissolved DCOD instead of total COD the presumption of DCOD following the water phase can be utilized. This simplifies the simulation significantly since no data on COD dividing properties is needed and all the DCOD can be assumed to divide proportionally to flow rates of water. All the "COD" marks in the model refer to DCOD. Unfortunately the name could not be changed afterwards without risking the model performance.

Literature provides the baseline that can be utilized as a guideline. Table 8 represents the literature findings used as guidelines in this work. The actual values used are represented at the end of this chapter.

Table 8 COD related parameters. Literature knowledge composes the baseline for modeling.

Equipment	**Equipment (TMP data)**	**K-value**	**Source**
	Disc filter		Lappalainen 2008 p. 51
	Colloids	1,5	
	Dissolved	0,7	
	Short circuit		Lappalainen 2008 p. 51
	Colloids	3	
	Dissolved	1,5	
	Wire press		Lappalainen 2008 p. 51
	Colloids	1,2	
	Dissolved	0,7	
	Equipment (CTMP data)		
	Screw press		
	Dissolved solids	0,98	Egenes and Barbe 1990 p.559
	Extratives	0,7	Egenes and Barbe 1990 p.559
Yield losses	**Yield losses in TMP**	**% in TOC**	
	Mainline refiners	2,1	Lappalainen 2008 p. 49
	Reject line refiners	0,5	Lappalainen 2008 p. 49
	Dithionite bleaching	0,5	Lappalainen 2008 p. 49

6.4 Formulas

6.4.1 COD (kg/mt)

COD in this work is a computational parameter that is assumed to be in 1:1 relation to dissolved wood solids. WinGEMS lets user to create new stream components (see figure 9) but their native units (kg/mt) cannot be modified hence other COD-components are required in order to create a functional model that is quick and easy to interpret.

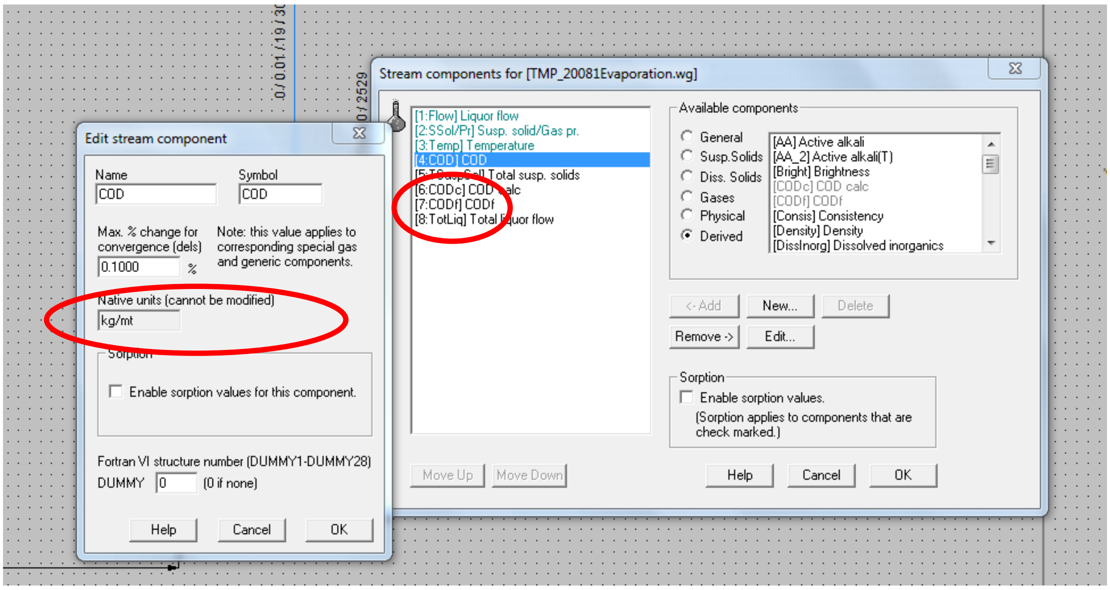

Figure 9 Stream compounds can be created from a ready-made list or from the beginning

6.4.2 CODc [mg/l]

COD analyses measure concentration (mg/l) thus related unit is required in simulation. This is performed by unit conversion: **CODc [mg/l]= COD[kg/mt]*1000** (see figure 10). Stream density is overridden.

$$
\begin{aligned}
&\frac{kg}{mt} \rightarrow \frac{mg}{l} \\
&\rightarrow \frac{kg}{1000\,kg} = \frac{1000 * 1000\,mg}{1000\,kg} \qquad |\, kg \approx l \\
&\rightarrow \frac{kg}{mt} = 1000\,\frac{mg}{l} \qquad (1)
\end{aligned}
$$

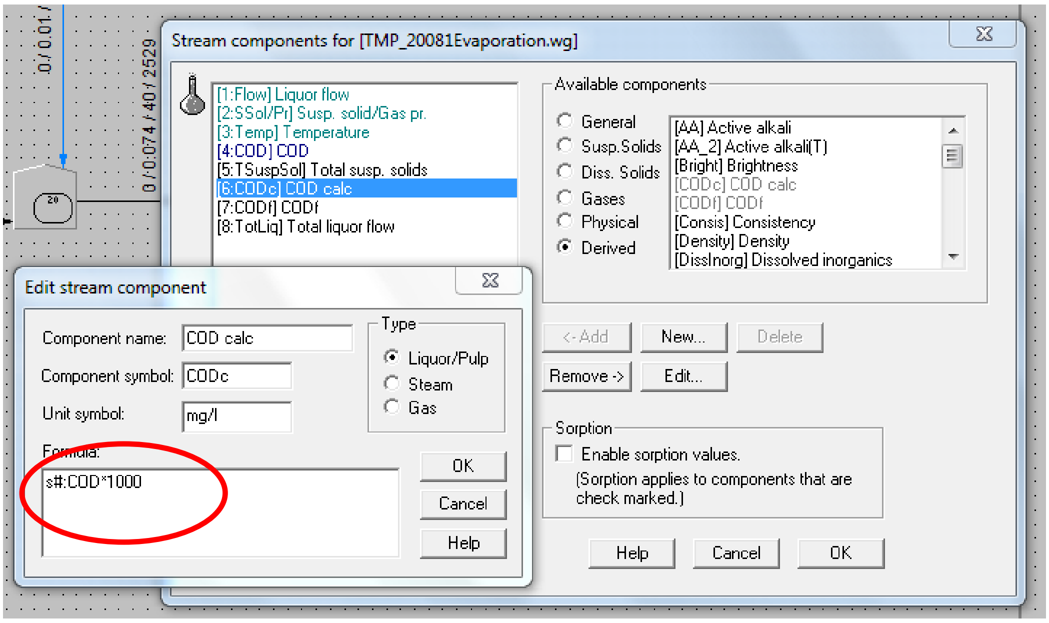

Figure 10 Inserting new stream component, CODc, to WinGEMS

6.4.3 CODf [g/min]

Simulator needs an unambiguous term to quickly evaluate COD balance accuracy in the model while working. These situations are continuous since simulator needs to have a clear view on how much individual equipment or chemicals add COD in the process. Mg/l is relevant since it is the unit of measurement data but as “a quick checking compound” g/min is better. CODf (g/min) takes flow rates in to consideration which enables balance check-up (such as, CODin=CODout). CODf is created by multiplying COD and total liquour flow (8th stream component in this model) and by unit conversion. Formula for CODf is then **s#:COD*s#:TotLiq*(1000/60)** (see figure 11).

$$
\begin{aligned}
&\frac{kg}{mt} * \frac{mt}{\cancel{hr}} \rightarrow \frac{g}{min} \\
&\rightarrow \frac{kg}{\cancel{hr}} = \frac{1000\ g}{60\ min} \\
&\rightarrow \frac{kg}{mt} * \frac{mt}{\cancel{hr}} = \frac{1000}{60}\frac{g}{min}
\end{aligned}
\tag{2}
$$

Total liquor flow (8th) is used instead of Flow (1st). Total liquor flow is Flow(1st) subtracted by Suspended solids(2nd) (8th=1st-2nd) thus TotLiq eliminates suspended solids from the flow. This is necessary since DCOD is assumed to migrate in the water phase thus only water (not suspended solids) are taken in to account.

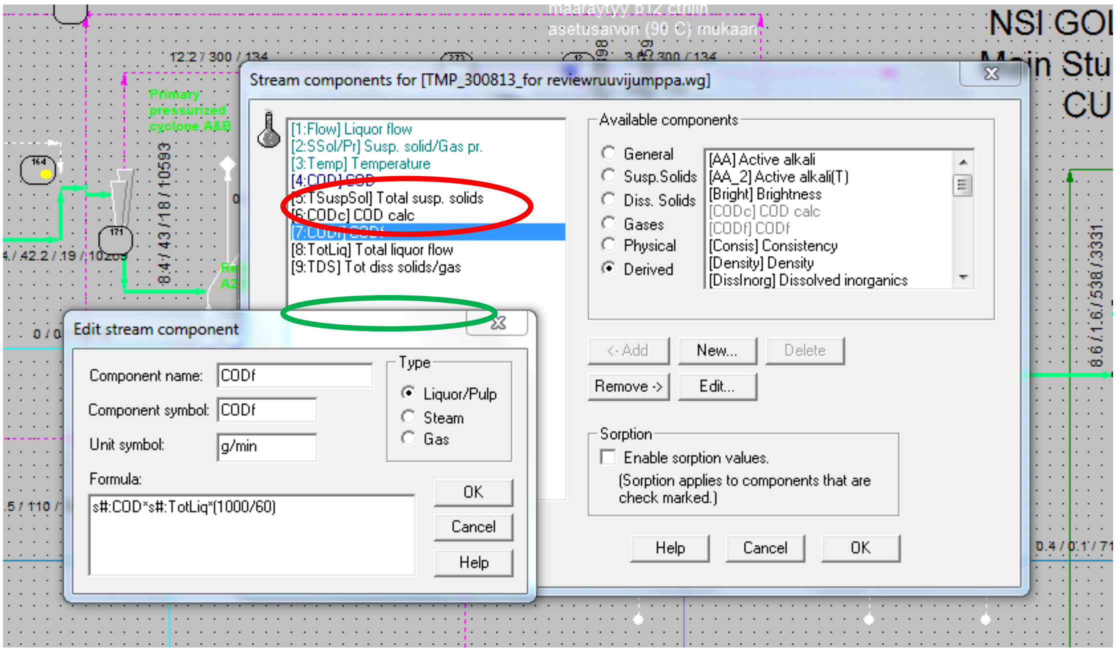

Figure 11 Inserting CODf to stream components

6.4.4 K-value

K-value represents the amount of how much dissolved and colloidal material transfers through dewatering equipment, such as disc filters and screws to paper machine. K-values describe the behavior of COD in equipment (see table 9) level thus this information is included in the model.

$$\boldsymbol{K_{COD} = \frac{c_{cake}}{c_{filtrate}}} \qquad (3)$$

, where K_{COD} K-value of dissolved and colloidal COD

c_{cake} Concentration of COD in the dewatered cake

$c_{filtrate}$ Concentration of COD in the filtrate (Lappalainen 2008)

7 RESULTS

Constructing the equipment in the COD-model requires conversion of literature knowledge to simulation logic. The following chapter represents the logic that was used in this work.

7.1 The COD-model of TMP

Most of the equipment was built from the beginning with *a compound block*-tool that is a custom block enabling user to choose just the specific characters and layout needed. Equipment was set to dissolve DCOD from the pulp or chips by *a reactor block* which connects the COD with production. Reactor based logic enables the automation: when production is changed the COD-balance changes accordingly. DCOD-balance in TMP is composed of:

- Dissolved wood solids released in the refiners and screws
- Carry-over from paper machine (The DCOD load transferring via make-up water is called *carry-over* in this thesis).
- Retention in disc filters.

However, this is a mere generalization thus all devices need to be studied case by case.

7.1.1 Refiner blocks

Refiner-blocks (see figure 12) used in this work are selected from the WinGEMS block library. User can define the refiner parameters and choose whether fiber loss appears or no. In this work yield loss is converted in proportion to DCOD. The DCOD composed in refiner 1 was 1.01 %.

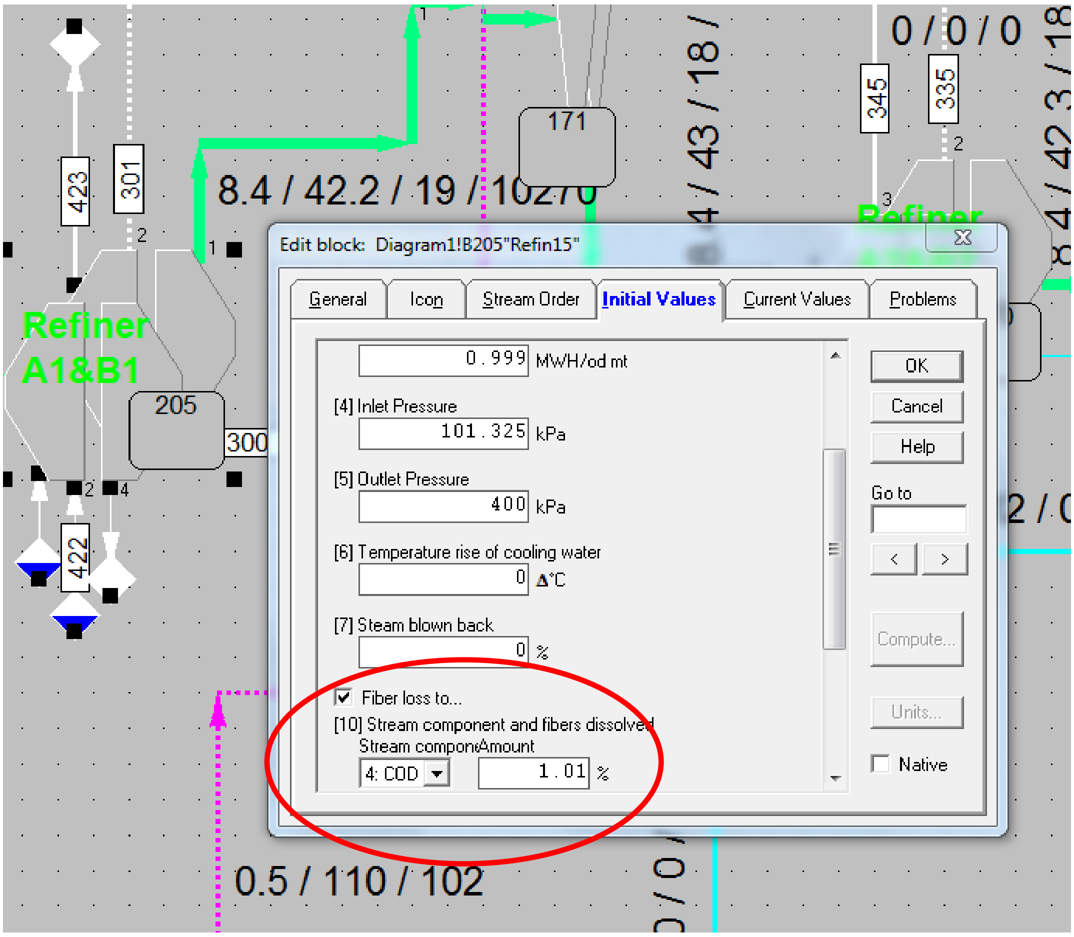

Figure 12 DCOD composing refiner (a ready-made) block

7.1.2 Make-up water

TMP process requires make-up water that in this case is produced from paper machine according to counter-current principle. Hence make-up water (in this study paper machine clear filtrate) transports DCOD from paper machine to TMP. Carry-over influences on DCOD-balance thus accurate water flow rate and DCOD concentration is vital. Figure 13 represents paper machine clear water (make-up) and whitewater (pick-up water) and heat exchanger whose water cycle is a closed loop between TMP and paper machine.

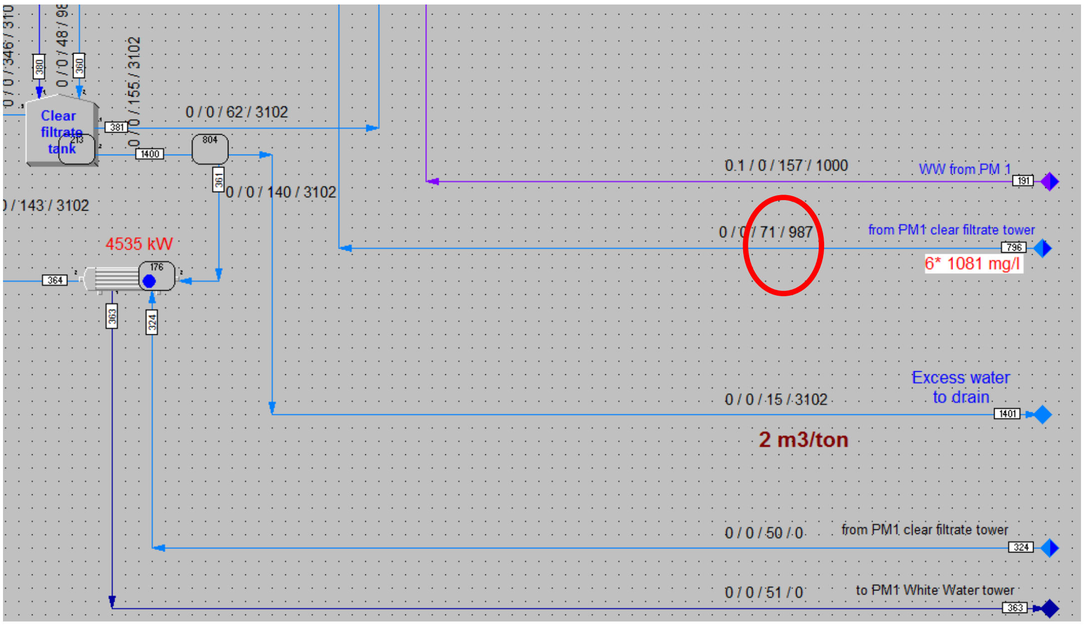

Figure 13 Make-up water transports 987 mg/l of DCOD, 71 l/s from paper machine to TMP. This is called carry-over in this thesis.

7.1.3 Screws

Dewatering screws and screw press in the beginning of TMP process seemed to compose DCOD according to measurement data thus DCOD producing reactor block was built inside of the screw block (see figure 14 and 15)

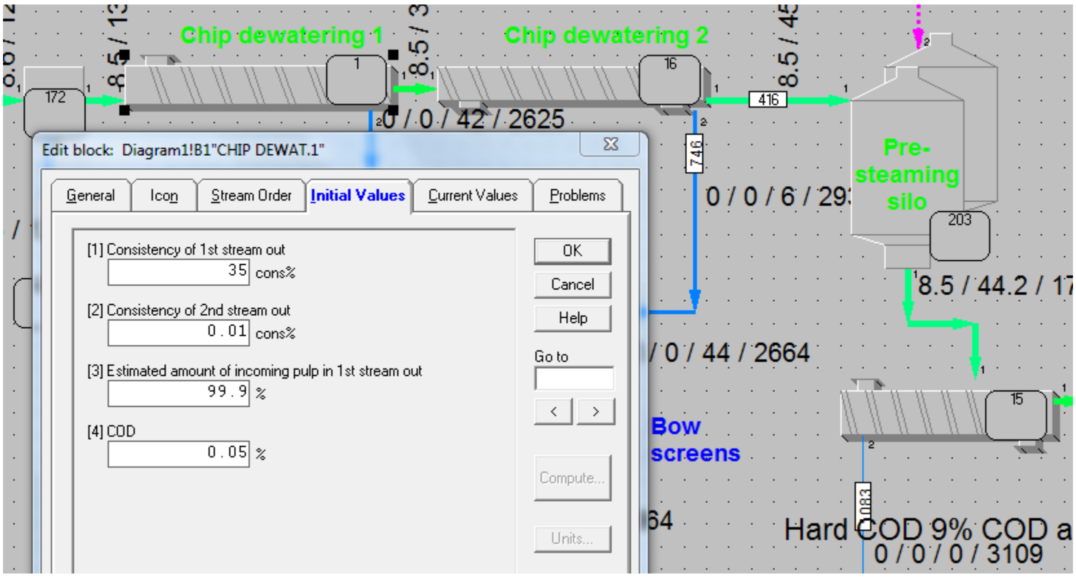

Figure 14 Screw blocks from the top level

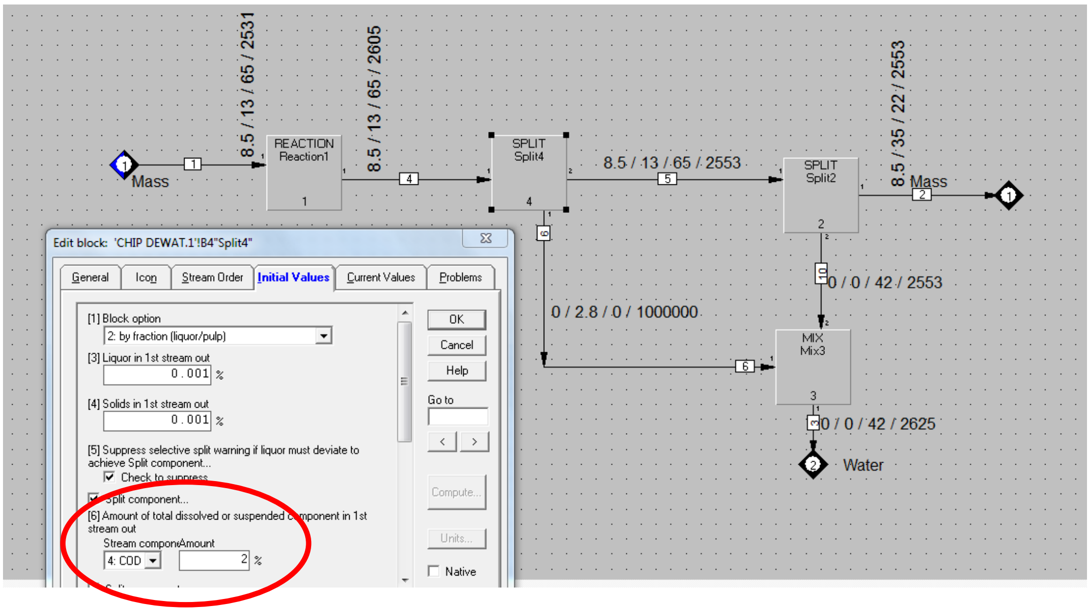

Figure 15 Screw block opened. Split 2 handles the basic screw functions (consistency adjustment), reactor handles the DCOD formation and Split 4 divides DCOD to filtrate and mass according to the measurement data (see the small window).

The layout of these screws may seem complicated but since one block (the screw in the parent level) needs to perform multiple functions (a. consistency adjustment, b. DCOD formation and c. DCOD division) several blocks had to be built to achieve required characters. In this case split 4 transports 2% of the DCOD directly to filtrate and Split 2 divides DCOD automatically by flow rate while adjusting the consistency. This way DCOD trend approaches the measurement trend.

7.1.4 Disc filters

Disc filter produce a filtrating mat of pulp that *can* retain few percent of DCOD. In this case greater concentration of DCOD was found in the filtrates than in the incoming mass (see figure 16). This indicates that disc filter in not functioning well.

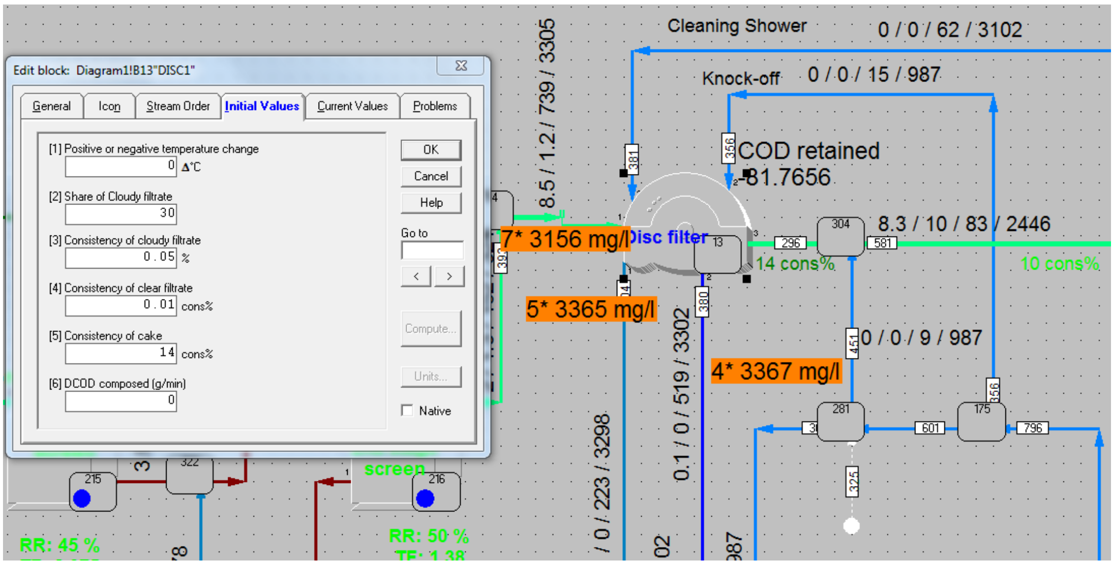

Figure 16 Disc filter main functions (consistencies and filtrate shares) are operated from the parent level

When modeling the “broken” disc filter user quickly observes that in order to achieve the measurement level in the filtrate alternative approach is required. In this case retaining of DCOD does not occur but additional DCOD leaks to filtrate. This is accomplished to the model according the figure 17. Split Mix1~2 and Split Mix1~3 divide the flow in pulp cake and filtrates (cloudy and clear). They also automatically divide the DCOD in proportion to flow rate. Additional DCOD leaking from pulp to filtrate is constructed by Split11 and Split 12. The first transports 5% of DCOD directly to filtrates and the latter divides this 5% to cloudy and clear filtrate according the measurements.

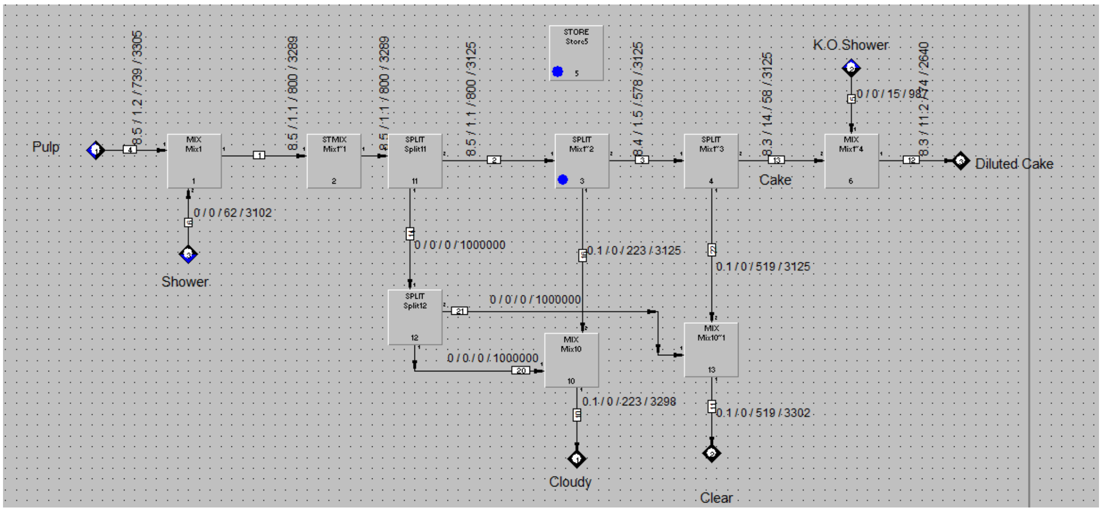

Figure 17 Disc filtrate divides water and pulp to multiple streams. In addition to basic functions, such as consistency, this disc filter divides DCOD by specific proportions depending on the stream.

7.1.5 Screens

Screens require close attention since the ready-made compound from WinGEMS library divides DCOD incorrect. Proportion according to flow rates was aimed but unfortunately the ready-made compound did not deliver as such. In this work Split compound was used and modified to screen properties (see figure 18)

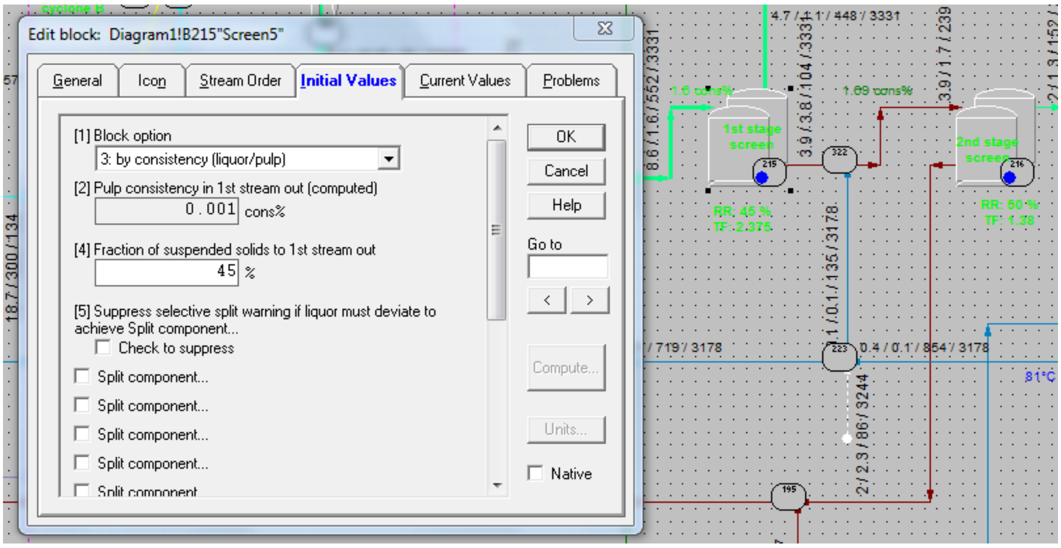

Figure 18 Screen compound is constructed from Split block in this thesis since the screen compound from the WinGEMS library divides DCOD incorrectly.

7.2 Paper machine

DCOD modeling in paper machine was simpler than in TMP since DCOD passes through within the water through most of the equipment. The next paragraph represents the two exceptions

7.2.1 Wire

DCOD retention is possible in short cycle but in this case measurement values were reached without any retention at the wire thus wire block is constructed to process only mass and water balance(see figure 19 and 20).

Figure 20 represents the blocks that form the wire functions. Four Split blocks divide the pulp mass into three filtrate flows and one mass flow. Mix blocks are needed to combine the shower water and other flows according the real situation.

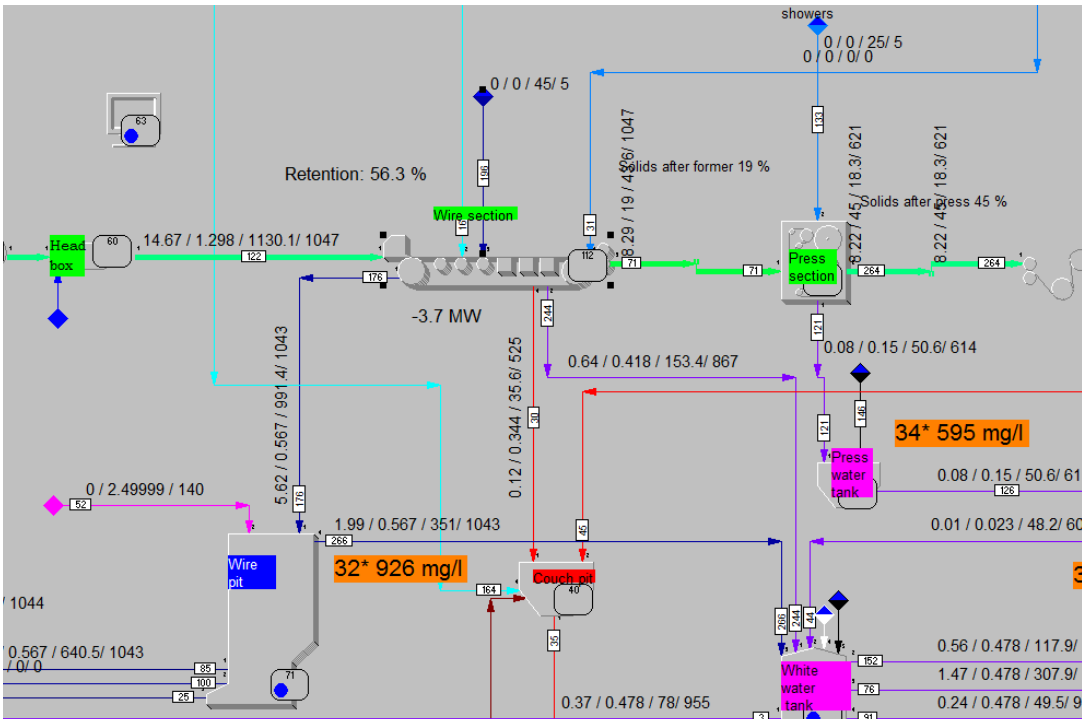

Figure 19 Wire block at the parent level

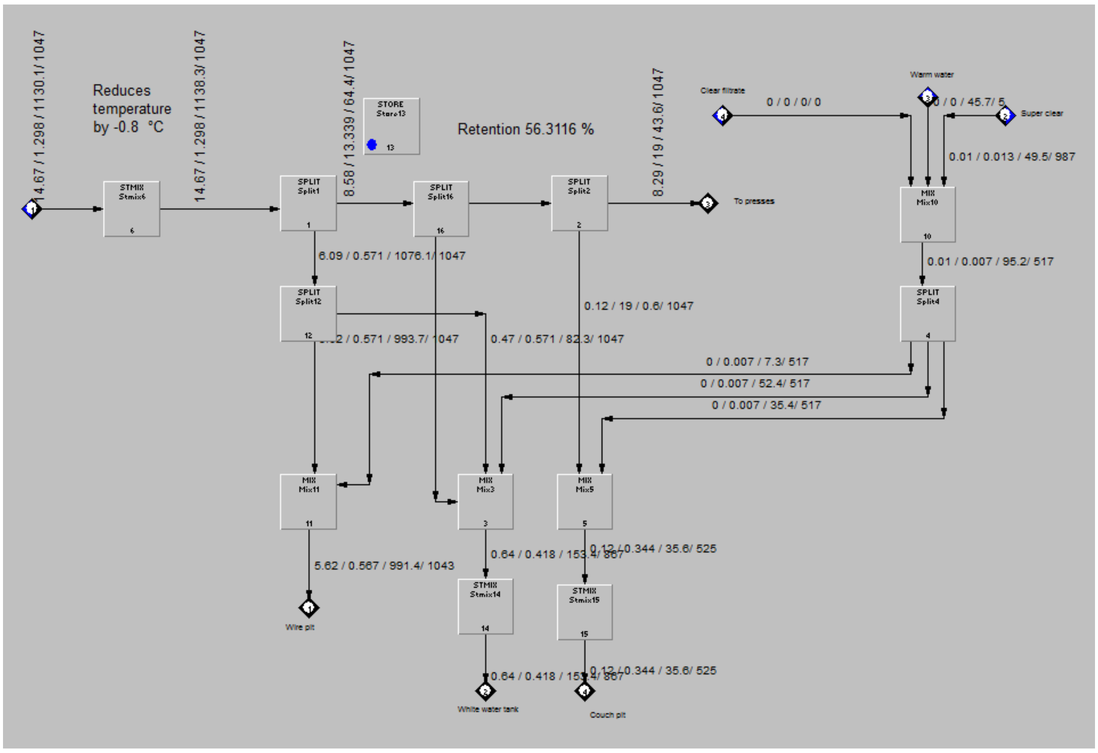

Figure 20 Wire block inside

The store block (see figure 21) is created to calculate and visualize the retention in the wire. This is implemented by a computation tool. User can feed a formula, in this case (s5:2-s13:2)/s5:2*100 that calculates the retention by subtracting the suspended solids in stream 5 and stream 13 and dividing the difference by suspended solids in stream 5. The result is naturally retention as percentage.

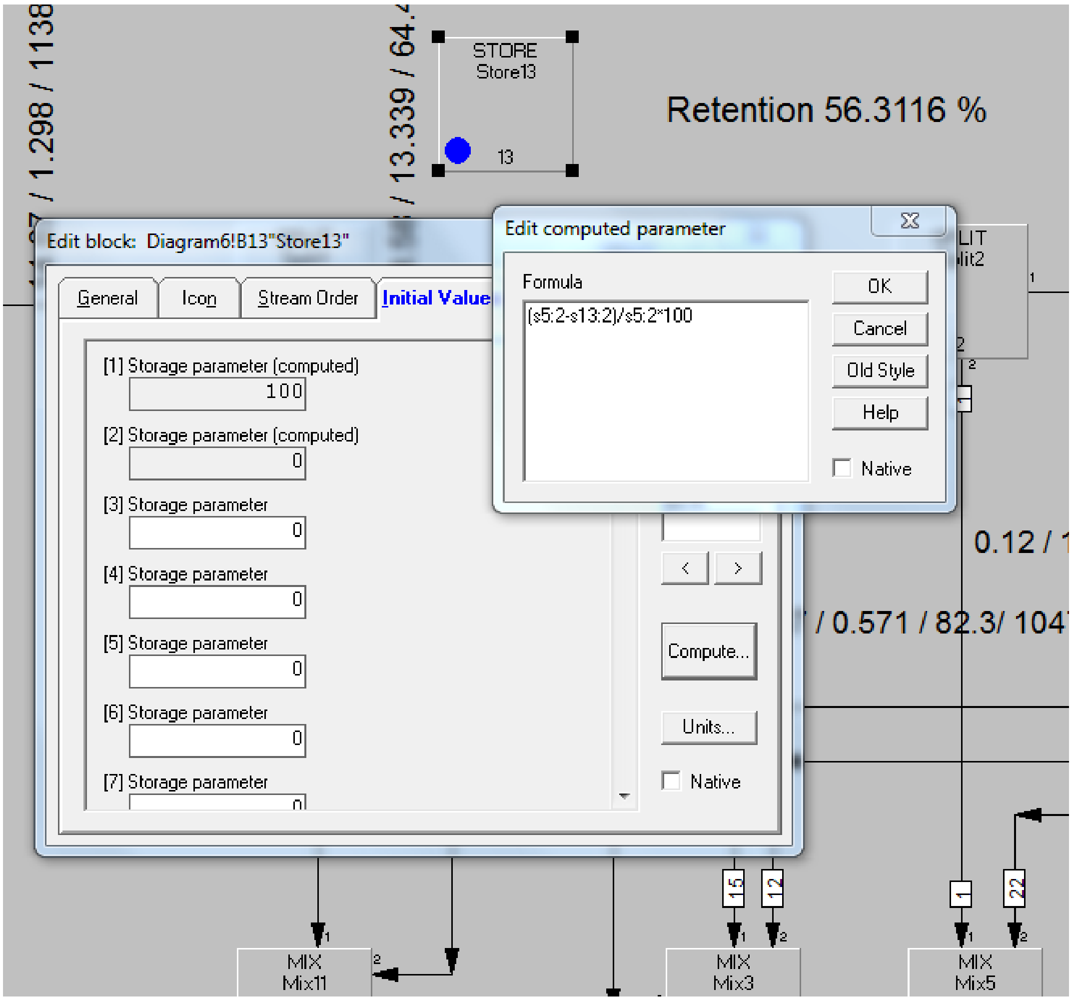

Figure 21 Store blocks can be used to calculate and visualize, for example, retention.

Texts in this work are usually constructed by formulas (see figure 22). In this case “Retention: %b63:5{d=1} %” which implies: print “Retention:” and the value from block 63 parameter 5. Command “{d=1}” denotes print the value to one decimal place. Accordingly, text change automatically when the model is modified.

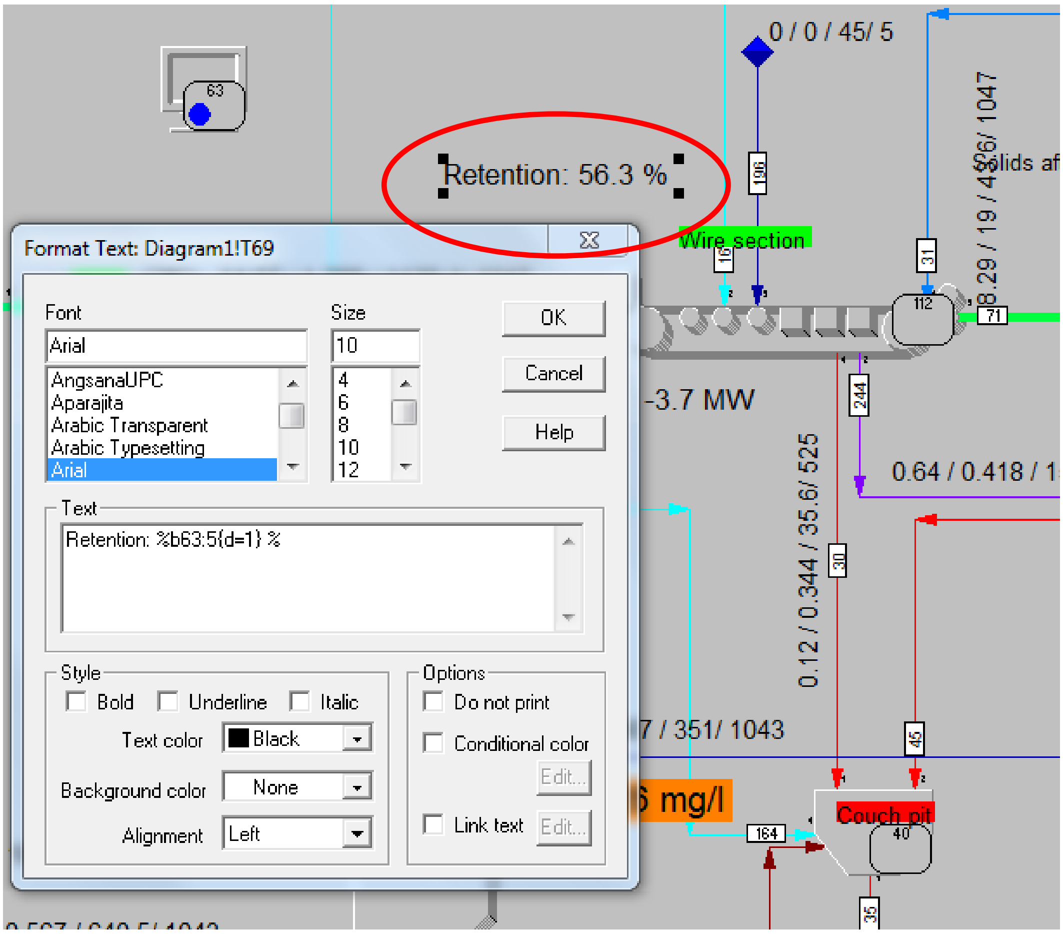

Figure 22 Texts are written by using computations. Hence the text changes according to the simulation.

7.2.2 Dissolved air flotation

Dissolved air flotation (DAF) is not an ideal method to remove DCOD but some reduction was achieved in the modeled mill according to the DCOD analyses. Hence DAF block is set to transfer 6% DCOD from inlet stream to sludge (see figure 23) resulting a 2% decrease in actual streams (from 614 mg/l to 602 mg/l). The drop according to measurement data is 2.4% in DCOD concentration (from 595 mg/l to 581 mg/l) but slightly smaller decrease was set due to literature findings of DCOD removal in DAF. Hereby a slight compromise between the measurement data and research values was performed.

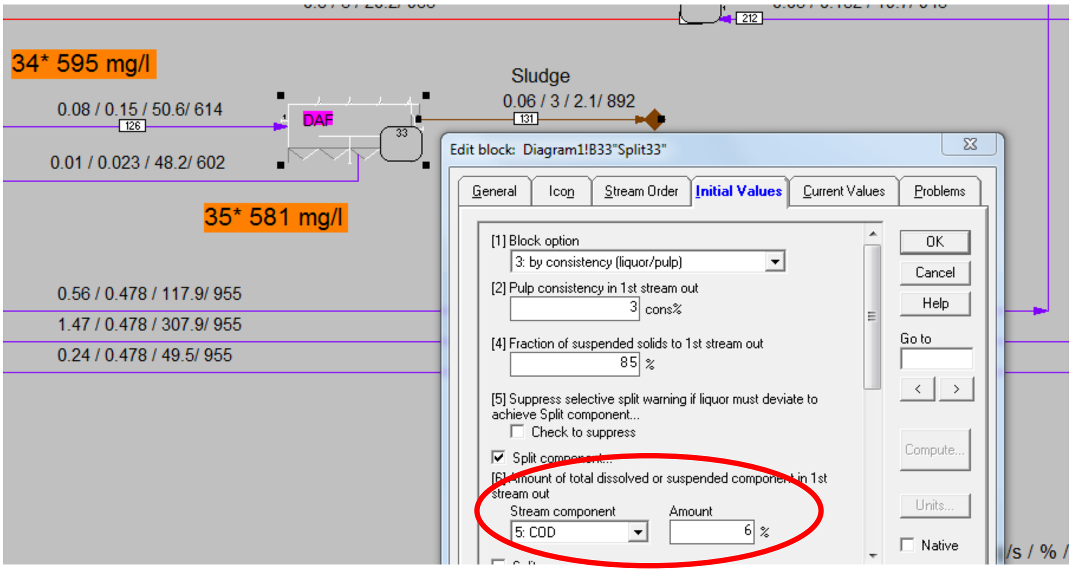

Figure 23 Measurement results showed a decrease of DCOD in DAF which was applied to the model.

8 DISCUSSION

8.1 Precision in the model

Precision is represented from three perspectives: 1) Fitting curve 2) Literature 3) Simplified Excel balance. The values represented in the following text are products of the certain mill and model thus should be used only to increase conceptual knowledge on DCOD in TMP and paper machine processes. Values can be generalized as starting point of iteration in other TMP and paper processes. Understanding the uniqueness of each mill and process is the key of simulation thus only the magnitudes of the values presented in this chapter can be generalized.

8.1.1 Fitting curve

Precision in the model increases by iterative process. First simulator adds values based on research or personal expertise and evaluates the results. In this work evaluation in iterative process was conducted with a fitting curve (see 24 and 25). Following section briefly describe the iteration process.

Initial setup

- Refiners were set to compose DCOD
- Carry-over via paper machine filtrates was introduced
- Disc filters were set to *retain* a few percent of DCOD *(notice that iterative process* indicated opposite and in final version K-value was set below zero)
- DCOD is assumed to transfer in water phase through the equipment

WinGEMS data can theoretically be exported to excel with add-in which allows examination of the overall accuracy and visualizes the changes in each iterative round. In this work accuracy was studied manually with the help of excel since the add-in did not work properly. Figure 24 demonstrates an early stage DCOD fitting curve.

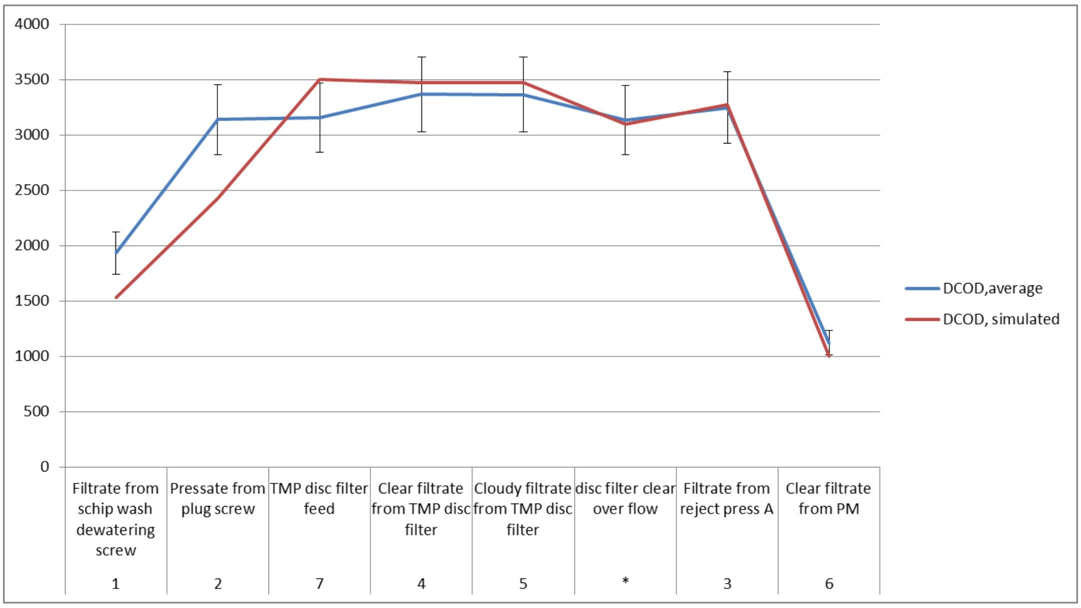

Figure 24 Increasing the model accuracy with fitting curve. The curve visualizes a clear difference in simulated and measured values thus pointing the areas that require further studying.

The blue curve represents the average measurement data and the red curve is the simulated value. As represented in figure 24 the early model produced decreased DCOD values at the beginning of TMP process whereas further in the process (the area of disc filter) the values were overly increased compared to measured values. Naturally, if the beginning of the process is manipulated to higher DCOD-values the rest of the process increases accordingly leading even greater inaccuracy. Hence the problem is in the DCOD division not in the amount. Example in question represents the whole concept behind modeling. Simulator needs to investigate why the model causes an incorrect trend. In this particular case the curves indicate that the screws in the beginning of TMP process require readjustment. The problem was fixed by adding the dewatering screws an ability to direct certain amount of DCOD within the filtrate (see figure 14 and 15). In other words DCOD is not divided according the water flow in the dewatering screws but mechanical force drives DCOD more in the filtrate than in the pulp. This phenomenon is also seen in the literature (see table 9: k- value is 0.98-0.7 for CTMP screw). After newly constructed screws the flaw was corrected.

Point by point the simulated DCOD-curve approaches the measurement curve and eventually needed accuracy is gained (see figure 25).

Final setup

- Refiners were set to compose DCOD
- Chip dewatering and plug screws were set to compose DCOD
- Chip dewatering and plug screws were set to transfer few percent of DCOD to filtrate (K-value below 1)
- Carry-over via paper machine filtrates was introduced
- Disc filters were set to transfer a few percent of DCOD into filtrate (K-value below 1)
- DAF was set to remove DCOD from the process
- DCOD is assumed to transfer in water phase through the equipment

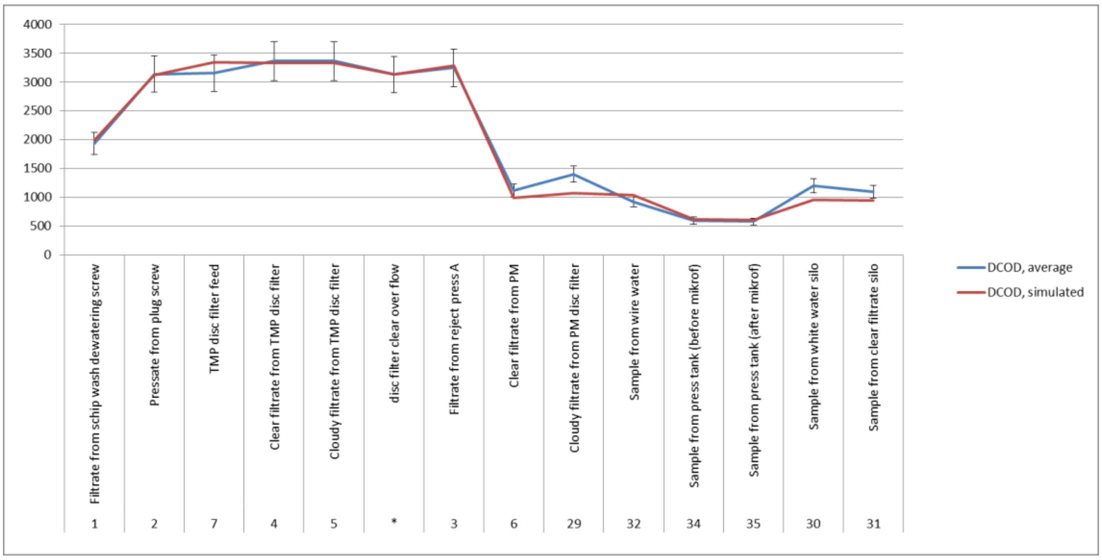

Figure 25 Modeled and measured DCOD values. See the graph in detail in appendix 2.

The fitting curve should be evaluated comprehensively and single measure points should not be overly focused (see table 9). Overall similarity between the trends is pursued over to single point accuracy for two reasons. Firstly, measurement results contain certain error limits due to measurement inaccuracy and secondly some results may be unconvincing thus critically managed.

Table 9 The percentage difference between simulated and measured values. The values in orange are evaluations due to lack of data.

	ID	Sample description	DCOD, average	DCOD, simulated	Difference, %	TOC	BOD	DCOD/TOC
TMP	1	Filtrate from schip wash dewatering screw	1933	1990	-3	740	940	2,6
	2	Pressate from plug screw	3138	3129	0	1500	1900	2,1
	7	TMP disc filter feed	3156	3341	-6	3000	3600	1,1
	4	**Clear filtrate from TMP disc filter**	3367	3338	1	1600	1600	2,1
	5	**Cloudy filtrate from TMP disc filter**	3365	3334	1	1600	1600	2,1
	*	**disc filter clear over flow**	3133	3136	0			-
	3	Filtrate from reject press A	3247	3285	-1	1600	1700	2,0
	6	**Clear filtrate from PM**	1122	987	12	470	680	2,4
PM	29	**Cloudy filtrate from PM disc filter**	1400	1071	24	670	430	2,1
	32	**Sample from wire water**	926	1041	-12	1900	610	0,5
	34	Sample from press tank (before mikrof)	595	613	-3	510	350	1,2
	35	Sample from press tank (after mikrof)	581	601	-3	230	200	2,5
	30	**Sample from white water silo**	1200	960	20	630	340	1,9
	31	**Sample from clear filtrate silo**	1100	950	14	510	390	2,2

Table 9 represents the percentage difference of simulated and measured values. Error limit in this work was set to 10% according to the systematic error of COD analysis used in client laboratory measurements. Points that exceed the error limit are highlighted in red.

8.1.2 Comparison between literature values to simulation values

Tables 10 and 11 represent modeled equipment in numbers and compare those with values from research. The concentration of DCOD increases in TMP process when wood dissolves into water. This is incorporated to the model by adding yield loss in certain components. For example Refiner 1 block in WinGEMS contains a parameter that converts 1.05% from total suspended solids into DCOD.

Table 10 Comparison of yield losses in the model and in the literature (Lappalainen 2008 pp.49-51)

	Yield losses in DCOD, %	In the model	Literature *	Difference
TMP	Dewatering screw 1	0,045		
	Dewatering screw 2	0,045		
	Screw press	0,01		
	Refiner 1	1,05	4,2	50 %
	Refiner 2	1,05		
	Reject refiner	0,5	1…1,4	50…64 %
	Total	2,7	3,6…6	25…55 %
PM	TMP bleaching	0	1	100 %
	DIP refiner	0	-	

* Lappalainen (2008) studied TOC yield losses in TMP which are converted to DCOD in this thesis based on the TOC and DCOD analyses performed by the mill personnel. According to measurements the coefficient is appr. 2 when converting TOC into DCOD.

Table 11 contains the K-values calculated from the model. WinGEMS does not contain K-value parameters thus K-value cannot be utilized automatically in WinGEMS simulation. In this work the lack of K-value parameter is overridden by building additional block structure (as seen earlier in chapter 7) those perform the operations of washing factor. K-values in simulation and in literature differ from each other. This can be explained by the unique characters of mills. The purpose of simulation is to study a specific mill thus producing mill-specific results. K-value comparison is performed in order to review and evaluate overall accuracy of the values.

Table 11 K-values calculated from the model and compared to literature.

	k-factor	In the model	Literature*	Difference
TMP	Dewatering screw 1	0,97		
	Dewatering screw 2	0,94		
	Screw press	0,87	0,98	11 %
	Disc filter	0,80	0,7...1,5	14…46%
PM	Disc filter	0,96	0,7...1,5	37…36%
	Short circuit	1,3	1,5...3	13...57%
		COD reduction, %		
	DAF	6,0		

*Lappalainen 2008 p.51

8.1.3 Excel balance

A simple excel TMP-model (see figure 26) was constructed in the early stages of WinGEMS modeling to evaluate WinGEMS results and functioning. Simplified TMP process was simulated using measured DCOD values and WinGEMS approximated flow rates. These values were used to check WinGEMS values and clarify the DCOD loads, such as carry-over, from certain points. Measurement results and WinGEMS flow rates enabled a quick and easy means to study DCOD carry-overs and magnitudes in the excel balance before the actual model excised. In addition the excel model increased the knowledge on equipment properties; whether DCOD transfers in proportion of water flow rate or in some other proportion. Rough estimation was achieved.

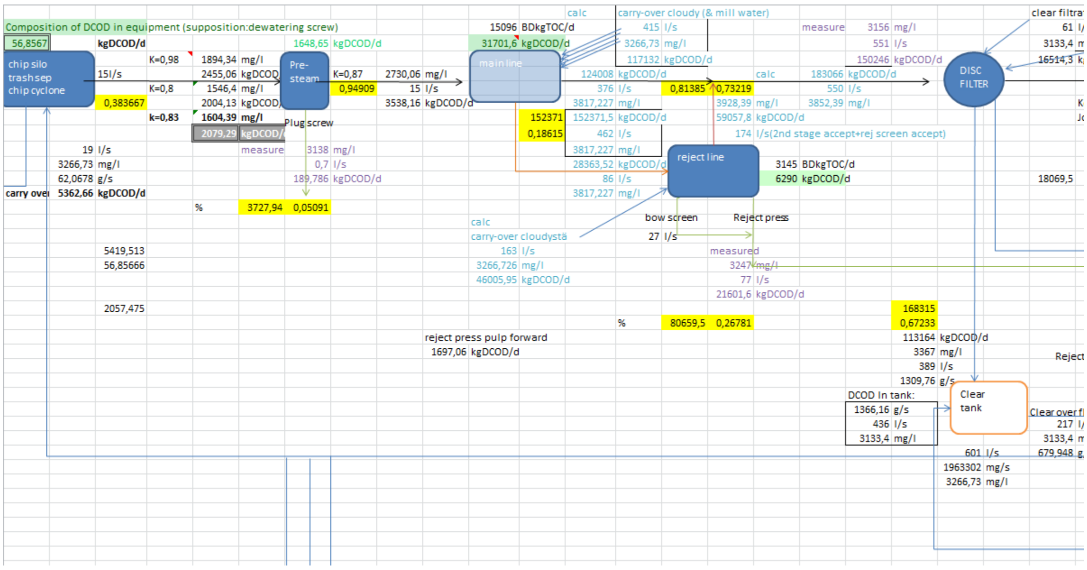

Figure 26 A snip of a simplified excel DCOD model used as an early checking tool and information seeking purposes.

8.1.4 Approved inaccuracy

Sample number 7 (DCOD in disc filter feed, TMP) was critically considered in this work. Analyses stated DCOD to be in average 3156 mg/l (1:3337 mg/l and 2:2975 mg/l) whereas the model filtrates indicated higher values. DCOD concentration is lower in the model disc filter shower waters which indicated that the filtrate concentration should be lower than the concentration in the feed. This is not the situation in the measurements. Balance calculations and the Excel model state the same trend than the model thus supporting the critical view towards measurement no 7. TMP disc filter feed (no. 7) is set over the measurement value to reach a mid-level in overall accuracy.

As represented earlier (table 2) each compound cause varying amount of COD when dissolving from wood. In this work it is assumed that dissolved wood (regardless of the specific compound) creates equal amount of DCOS hence dissolved wood: DCOD is 1:1.

Modeled K-values and yield losses differ 11 to 100 % from literature values. In this work literature values were not aimed but unique, factory-specific DCOD-balance was targeted. Hence literature values were utilized only as initial values of iteration.

8.2 Critical review

8.2.1 Unreliable PM model

TMP and PM models are contrasting examples: TMP model fitted logically on measured values and produced accurate results whereas PM model fitting curve worsened if logical actions were implied.

A variety of reparative means was conducted to increase PM accuracy:

- Bleaching tower was set to compose DCOD from dissolving wood
- DIP refiner was set to compose DCOD
- DCOD retaining compound was added in wire-block
- Press section was set to transfer few percent of DCOD to filtrate (K-value below 1)
- All the other settings mentioned in earlier version

Reparative actions increased the overall inaccuracy to the point that only unrealistic methods would have corrected the trend. It seemed that not all the measurement values were logical. For example, if PM clear and white water concentration is really as reported the press water concentration cannot be that low. PM was drastically lacking usable measurement data thus tracking the unreliable values was challenging. In addition points 29, 30 and 31 are only evaluations based on total COD, calculations and other measurement data thus may contain errors. The values in the PM water flows were critically judged since the results were illogical. Number 6 (Clear filtrate from PM) and 31 (Sample from clear filtrate tower) *should* contribute approximately same concentration since they are the same flow. Measurement data reports great difference between the samples (TOTCOD 31: 1448 mg/l, 6: 7291 mg/l) which is highly illogical. PM model did not reach approved level of accuracy thus explanatory measures are required to conduct both models to explicit level. Additional DCOD measurements from PM process are required to gain understanding and recognizing false values.

As represented above, PM model baseline data was drastically lacking trustworthy measurement values thus simulating was challenging and resulted as poorer accuracy in PM model (see in figure 25). Supposedly, two greatest errors in PM model are: 1) 34 and 35 illogically low compared to overall concentration and wire water concentration. Such a trend requires unrealistic amount of retention in wire and press section. 2) The model has deficiencies in water schema. Possibly water flows with low concentration are controlled in the mill differently than represented in the model thus the model layout has errors. With these dilemmas in model accuracy PM simulation is unreliable and requires further investigation.

8.2.2 Shortage in water balance

Both models comprise a deficit in water balance since some inputs and outputs are not related in to production which is the greatest shortage of the models. The models were constructed to mimic a certain paper mill at certain level of production thus known fixed purge and inlet values suited well in this thesis but stagnant values hinder the simulating capacity of future scenarios. In the old mills flow meters are rare thus flow rate data was challenging to collect. Due to lacking water flow rate data possibilities to model many water related scenarios is decreased. Many environmentally interesting indicators relate to water consumption which highlights the importance of this drawback.

8.3 Challenges in WinGEMS

Pöyry requested information from the COD-modeling procedure. This chapter represents the most important challenges and observations from the simulation process.

The challenges emerge from two standpoints. Firstly, many of the problems described in this part emphasize the challenges a beginner modeler may encounter. WinGEMS is not maybe the easiest program to learn by one self since user base is rather limited. Consequently, no help from the internet is available. Metso offers a help service by e-mail (in response time of three days) but several contacts unfortunately led to nowhere. WinGEMS seems to contain many features that a beginner stumbles upon. Secondly, the challenges represent some difficulties that hinder the possibility to share and exploit ready-made models inside Pöyry. To increase the possibility to utilize or develop a shared model base these challenges should closely be attended. Following section compiles some challenging features or so called stumble blocks prevailing in WinGEMS.

8.3.1 Transparency

i) Figure 27 demonstrates one of the problems concerning the lack of transparency. This example block contains 1-15 “Storage parameter” (of which 9-14 is seen in the screen shot) many of those containing a computation. Models contain tens of the blocks and calculations described above which forms model examination laborious if explanatory texts are missing.

Guideline: “Storage parameter” should be changed to explanatory name by double clicking.

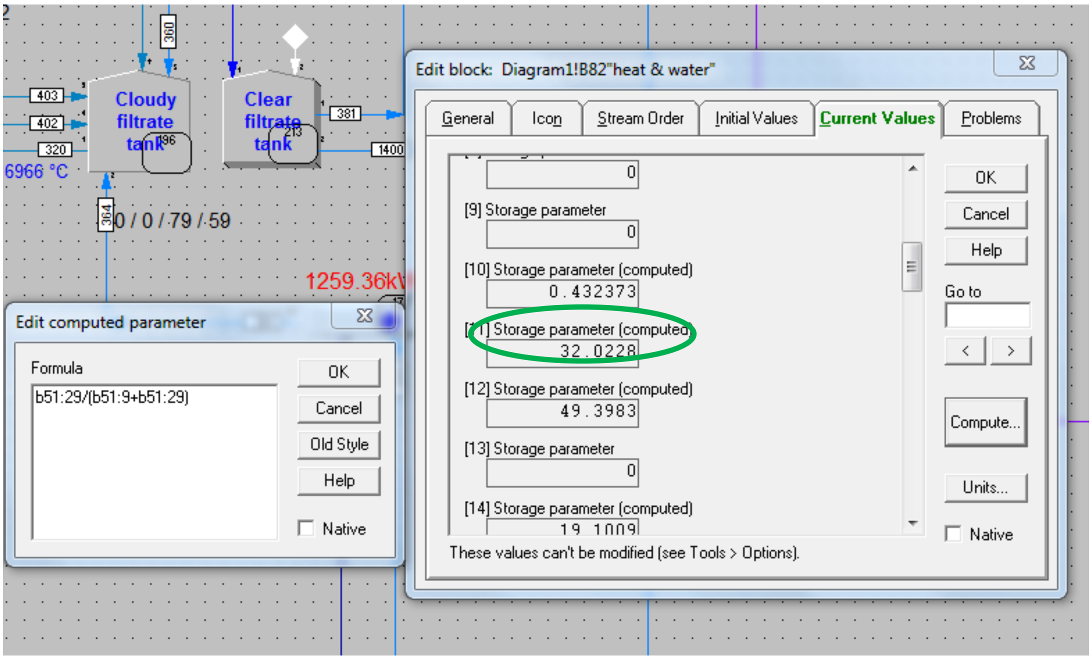

Figure 27 Adding explanatory texts to each parameter benefits when models are constructed in shared library.

ii) Water balance gets invariably imbalanced during the model construction. Changes in model layout or equipment properties cause water balance to produce inaccurate results. Figure 28 represents the checking balance calculations of a model with this problem.

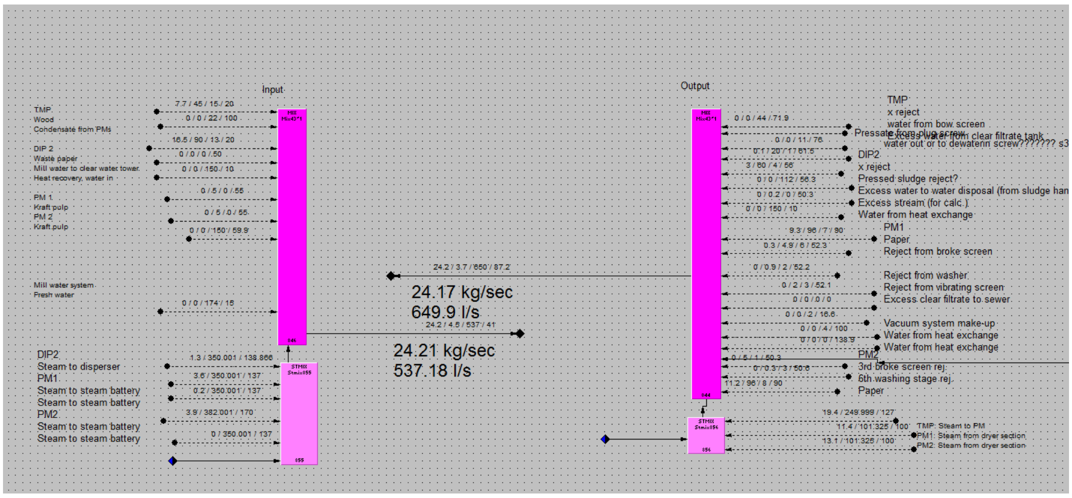

Figure 28 Water balance show a difference over 100 l/s between input and output flows

Imbalance occurs since dilution blocks start to create additional water within the process to achieve control settings or some blocks bleed water out of the system. One can imagine the task of locating the “broken” dilution block from vast models (see figure 29).

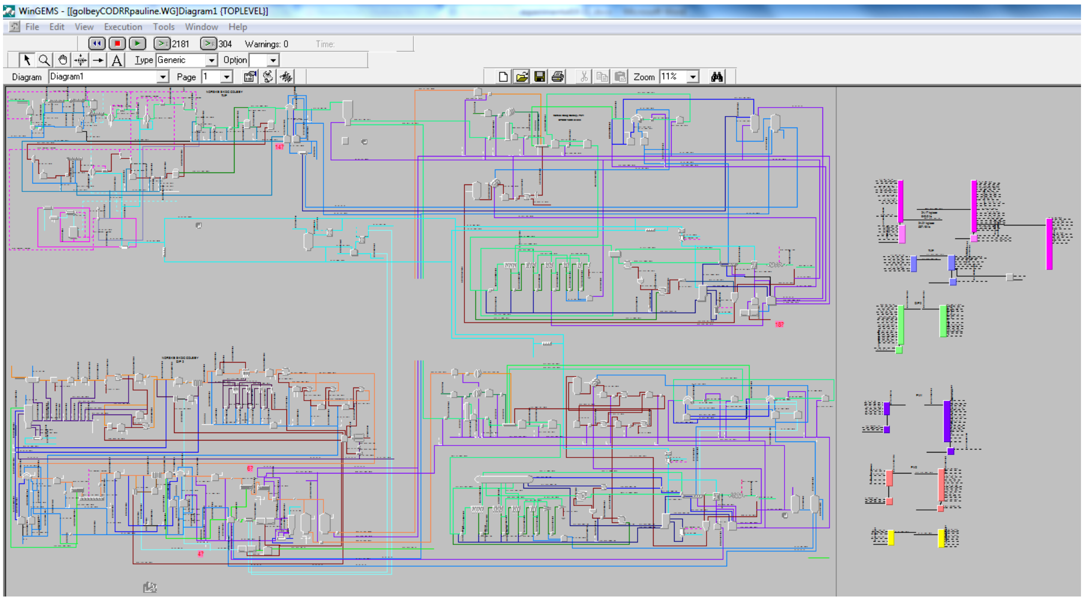

Figure 29 Example of an extensive model

Usually the “broken” blocks are in the end part of long water stream (see figure 30)

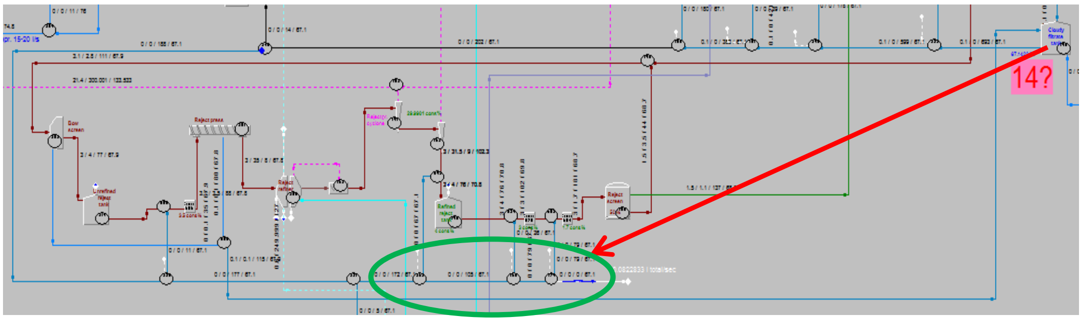

Figure 30 Water is directed through many blocks and often those final blocks contain dysfunctions. This block bleeds water incorrectly out.

***Guideline*: Balance check-up (see figure28) is required to reveal errors.**

8.3.2 Fixed values

Models are constructed to reflect a specific mill which easily leads to a simplifying conclusion of setting controllers with known, fixed values. For example, simulator happens to know that clear water overflow in modeled TMP is ie.15 l/s at the production rate the TMP in question is usually driven. The model functions well in the steady environment but what occurs if later this model is used to investigate the outcomes of new production rates? Fixed value will offer the same set value which highly diminishes the ability to generalize, manipulate and investigate with the model! The danger of using fixed or manual values is the fact that minute details may easily be left unnoticed thus the risks to wrong interpretation increase.

COD can be added to the model by using fixed values (compare the style used in this work where COD is a production related parameter). The task of localizing all the fixed “COD injections” is challenging which leads easily errors when developing the work of some-one else´s.

8.3.3 Data importing

The scarcity of functions in WinGEMS hinders the value of the software, for example depletion of capability for data processing and graphical analyzing is a major deficit. Excel add-in would compensate if the tool worked properly. Regardless of several attempts WinGEMS 5.3 refused to open in Excel 2010. Data reports can be printed from WinGEMS as .txt-file but the data can´t easily to be exploited in Excel (the data is printed in confusion thus arranging is overly laborious). Supposedly, this is the reason why WinGEMS add-in character is developed. Unfortunately, add-in tool just doesn´t work properly in Excel 2010 which is a major deficit since data processing is important especially when simulating various scenarios or evaluating the model accuracy. This work consisted massive amount of work since all the data had to be manually transferred.

8.3.4 Challenges of beginner user

This work contains some first timer´s decisions that complicated the process and created unnecessary imprecision. The following presents these point by point in order to clarify better procedure to conduct a COD balance in the future.

i) Initially COD analyses were requested from total 21 points but some critical were missing. In addition total COD was prioritized and DCOD wasn´t requested in all the sampling points. This was a major error since some flows had to be evaluated using other process water and effluent data provided by the mill personnel. This is time consuming and produces error that could be avoided by better sampling selection. ***Guideline*****: Model DCOD. If total COD is required, measure the COD content in SS and use that information to calculate the total COD in the model.**

ii) Building a functional model preceded multiple versions. One of those was a model were multiple separate levels was utilized. In this model all the mill departments were linked *and controlled* from the top level while the actual departments function beneath the blocks (see figure 31 and 32). The reason to link all the departments together was to construct unity and increase automation. Advanced characters are achieved when the whole mill is controlled from one point since every alteration affects automatically on every department. In addition the visual outlook is cleaner thus simpler to understand. Unfortunately, complexity creates complex challenges. Despite several efforts the controllers in the top level didn´t work according to their commands. Another great problem was the difficulty to alter the departments once fixed as an entity. Apparently the calculation logic didn´t support the controller decisions or some unknown errors affected causing unwanted behavior. Hence the united model was abandoned and simpler individual department models were created. In this thesis one paper machine and a TMP is represented. ***Guideline*****: Aimed complexity need to be optimized with the skill of simulator and available resources.**

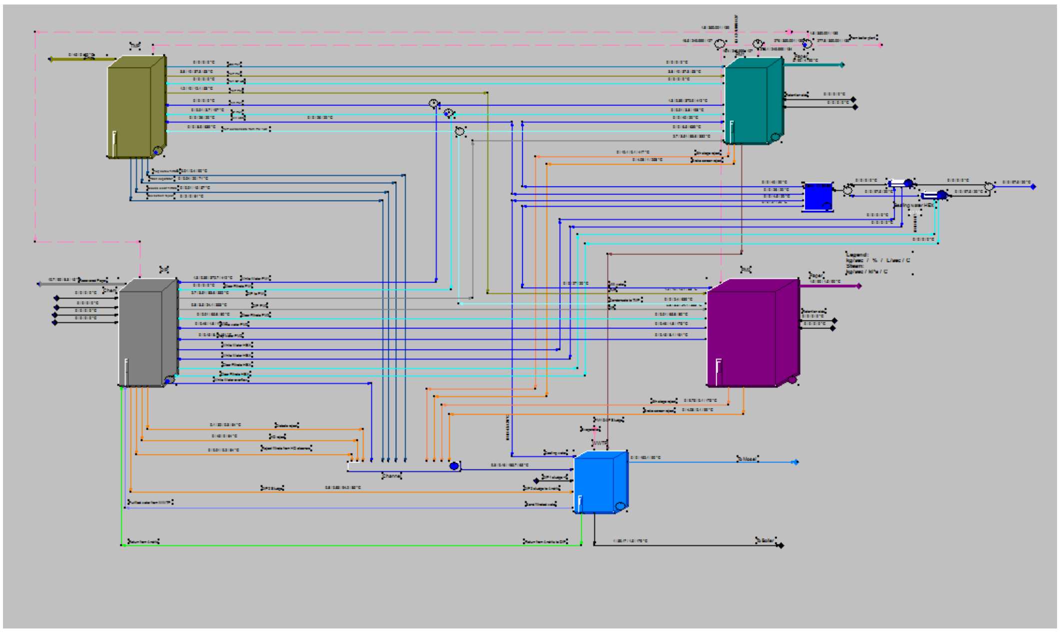

Figure 31 The highest level contains all the mill departments and their connections. These blocks contain each a full department model within (see figure 32)

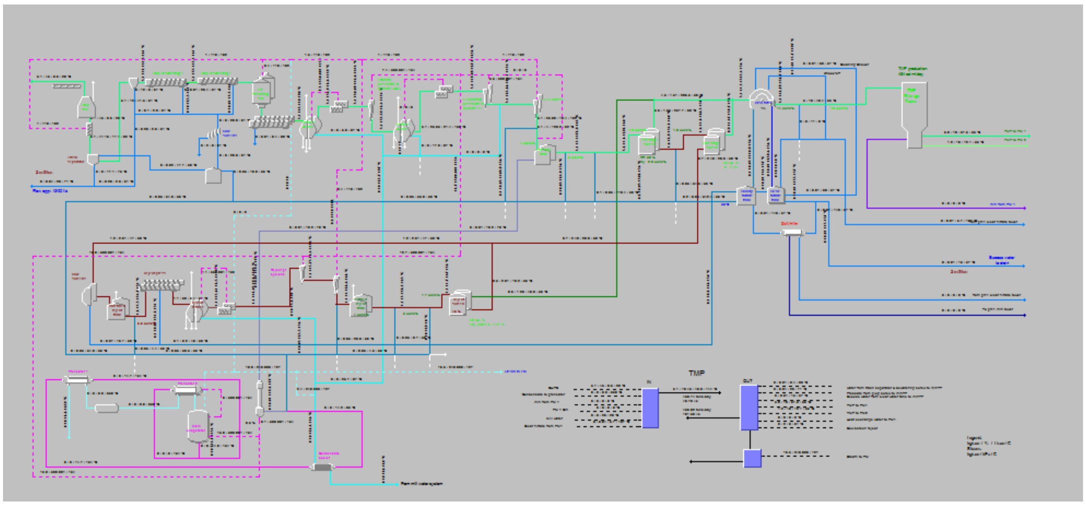

Figure 32 Compound blocks can be created complex. This TMP is content in one of the blocks seen in figure 31

9 CONCLUSIONS AND RECOMMENDATIONS

Literature part approached COD in thermomechanical pulping plant (TMP), deinked pulping plant (DIP) and paper machine (PM) by characterizing the compounds in the departments. Dissolved and colloidal substances (DCS) are studied due to COD characterization. They are important also since attempts to reduce water consumption result in accumulation of these substances thus i) increasing COD load and ii) producing various problems in the process. Removal of COD was studied in the light of water reduction thus this work concentrated on internal kidneys. DCS in TMP is abundantly researched while the other departments lacked research, especially PM. Particularly, COD potentials of paper making chemicals should be further investigated. This subject should be approached by studying a chemical after another since characterization of paper machine white and waste waters is not researched. This is probably due to fact that paper machine process waters are cleaner than the waters at pulping plants but when aiming reductions in water consumption enhanced knowledge on all process waters is required in order to better exploit the effluent flows as process water. Characterization (5-component fractionation) was studied in this thesis since a sum parametric COD alone is insufficient means to discover information from detrimental contaminants in process waters. Majority of DCOD consist of carbohydrates in TMP, lignin in DIP and probably from the both in PM process waters. Optimal removal of COD and technical realization highlight the importance of knowing the characteristics of waste waters/effluents. Identification of COD fractions and quantitative knowledge enable to adopt the technical solutions with maximum benefit that leads to more efficient and cost-effective water treatment, optimal operation and empowers modeling of future scenarios. Process water treatment design and planning should be based on the individual characteristics of the process waters rather than on an assumption of universal water.

Two models containing mass, water and DCOD-balances were constructed and evaluated in the experimental part. Close co-operation with mill personnel was required to achieve equivalence of TMP and paper machine models and the actual mill. DCOD-balance was constructed by investigating the overall level of DCOD in the model. In other words overall precision was prioritized over aiming specifically the measured values. Hence this work started developing DCOD-model strongly relying in *factory-specific* DCOD analysis which was performed in practice with fitting curve that enabled the comparison between measured DCOD-values and simulated DCOD-values.

Accuracy of DCOD-models was evaluated by the fitting curve whose error limit was set to 10% according to equivalent to the error limit of the DCOD analysis performed by the mill personnel. DCOD fitting curve fitted almost perfectly to the TMP model and reasonably well in PM model: The difference between measured and simulated values varied between 0 and 12 % in the TMP model and between 3 and 24% in the PM-model. Yield losses varied between 25 and 100% and K-factors between 11 and 57% in TMP and PM-models. Percentage difference may seem great but is explained due to unique characteristics of each mill. The overall approach of fitting curve is an attractive method of modeling COD since the approach takes the uniqueness of the mill into consideration. COD-model is constructed then from the standpoint of the certain factory. Thus specific and detailed COD-analysis is a necessity to create an accurate and mill-specific COD-model. As seen in the variations of literature yield losses and k-factors generalization of the results directly to other TMP and paper machine is not possible but numerical magnitudes can be exploited. Under the studied criteria the models performed fairly well. In the model of PM the number of available measurement points was limited since critical studying of the results is necessary. Accuracy could be enhanced by including several components, such as ash and stickies, in addition to DCOD. These “tracer” groups could be exploited by optimizing multiple fitting curves. Even though enhancing accuracy is highly recommendable simulator requires optimizing available resources and complexity of the model.

Even though both the models are fairly accurate two great deficits was recognized. Firstly, both models contain a deficit in water balance since some inputs and outputs are not related to production but set to certain known values. This is the greatest shortage in the models. Setting the model to reach certain fixed values serves the purpose of building a model similar to real mill but the technique hinders the simulating capacity: not much can be simulated if the model reaches the same values regardless of the situation. Models are created to investigate the change. This purpose isn´t reached if the simulation logic is based on stagnant situation. The aim was to construct the models to mimic a certain paper mill at certain level of production thus known fixed purge and inlet values suited well *to this thesis*. The problem arises when the model is utilized to predict future scenarios. Utilizing of fixed values in this thesis was due to lack of water flow rate data which is a common problem when working with old mills. Investigating the flow rates of the greatest process water purges and inlets with few alternative production rates is highly recommendable since this offers the overall view of water trend fluctuation. In the case of old mills this designates manual flow rate measuring. Flow rates of mass flows are better available from process control system views thus only water flows should be manually measured. In the case of newer mills flow rate is monitored with online meters thus the water trends can be obtained and exploited in simulation. In the future water balance should be connected in relation to production. Secondly, PM model baseline data was drastically lacking trustworthy measurement values thus simulating was challenging and resulted as poorer accuracy in PM model than in TMP model. Due to defective data PM simulation is unreliable and requires further investigation.

WinGEMS has deficits in usability. Firstly, exploitation of shared model library is challenging since WinGEMS is lacking transparency and explanatory space hence understanding of the content is time-consuming. Secondly, WinGEMS is lacking customer support and contains various computational challenging that hinder efficiency of beginner users. Thirdly, the scarcity of functions in WinGEMS hinders the value of the software, for example depletion of capability for data processing and graphical analyzing is a major deficit. Excel add-in would compensate if the tool worked properly. Due to these shortages question remains open weather WinGEMS is the most suitable software for Pöyry. Model scope, complexity and accuracy vs. price are a point to be carefully examined in the future projects. Accessible and user-friendly model library would be an ideal solution to diminish the workload of simulation. Unfortunately, it seems that WinGEMS cannot provide co-used model base. Other possibility could be unified training if WinGEMS is utilized in continuation. WinGEMS training should aim for unity, for example, controllers are built in the same logic, explanations for parameters and text descriptions are included. Primarily I recommend that other simulation software is reviewed and education for selected common software is organized in order to exploit all the potential simulation tools can provide.

Simulation of this work could be developed by uniting the departments as one model. Consequently, changes in one department would automatically result in other departments. For example increase in paper production in one paper machine would automatically cause increase in chip inlet, water purges and demand etc. Hence manual work and chance for human error are drastically diminished. Unfortunately, model complexity can create complex problems. Simulator must optimize complexity with his or her know-how.

10 SUMMARY

Stiffening environmental regulations claim to efficient management of water contamination. Exact knowledge on the process waters and effluents enable tailor-made process water or wastewater treatment thus enhancing the control and management of water contaminants. Process designers should aim for recognizing and removal of the detrimental components. Dissolved COD is challenging to remove but by analyzing the detrimental components optimal treatment methods can be selected. Simulation can be efficiently used to serve water contamination management and control. COD models of thermomechanical pulping plant and paper machine were constructed with Metso´s WinGEMS 5.3 simulation software in this thesis. Accuracy of DCOD-models was evaluated by the fitting curve whose error limit was set to 10% according to equivalent to the error limit of the DCOD analysis performed by the mill personnel. DCOD fitting curve fitted almost perfectly to the TMP model and reasonably well in PM model: The difference between measured and simulated values varied between 0 and 12 % in the TMP model and between 3 and 24% in the PM-model. Yield losses varied between 25 and 100% and K-factors between 11 and 57% in TMP and PM-models. Percentage difference may seem great but is explained due to unique characteristics of each mill: COD-model should always be based on measurement values of the particular mill not example values form literature. The overall approach of fitting curve is an attractive method of modeling COD since the approach takes the uniqueness of the mill into consideration. As seen in the variations of literature yield losses and k-factors generalization of the results directly to other TMP and paper machine isn´t possible but numerical magnitudes can be exploited.

Even though both the models are fairly accurate two great deficits was recognized. Firstly, both models contain a deficit in water balance since some inputs and outputs are not related to production but are set to certain known values. This is the greatest shortage in the models. Secondly, PM model baseline data was drastically lacking trustworthy measurement values thus simulating was challenging and resulted as poorer accuracy in PM model than in TMP model. Due to defective data PM simulation is unreliable and requires further investigation.

COD modeling is rather complex as a procedure. This work contains pointers how to accelerate the process. “The task list of a simulator” represents the procedure point by point.

The task list of a simulator

1) Gather data of process, process waters and xx philosophy *at specific production* with simple and unambiguous methods (e.g. formulates). Process control system views and other flow rate data must be from the day of sampling day.
2) Gather numerical data from literature on COD in relation to the specific process
3) Convert literature knowledge into simulating logic.
4) Check manually the correctness of created formulas and overall correctness of the model.
5) Check the mass and water balances with checking balance calculation (inlet and outlet flows must be equal: conservation of mass). Remember to take yield loss into account.
6) Evaluate the model with fitting curve and literature knowledge.
7) Modify and evaluate critically the model point by point.

This thesis represents effective method and baselines for COD modeling of TMP and paper machine which can be generalized to other mills and departments. The method of fitting curve serves efficient and fairly accurate method for COD modeling if sampling point data is sufficient. Including a production based water balance and uniting the departments as one entity is strongly recommended for further development.

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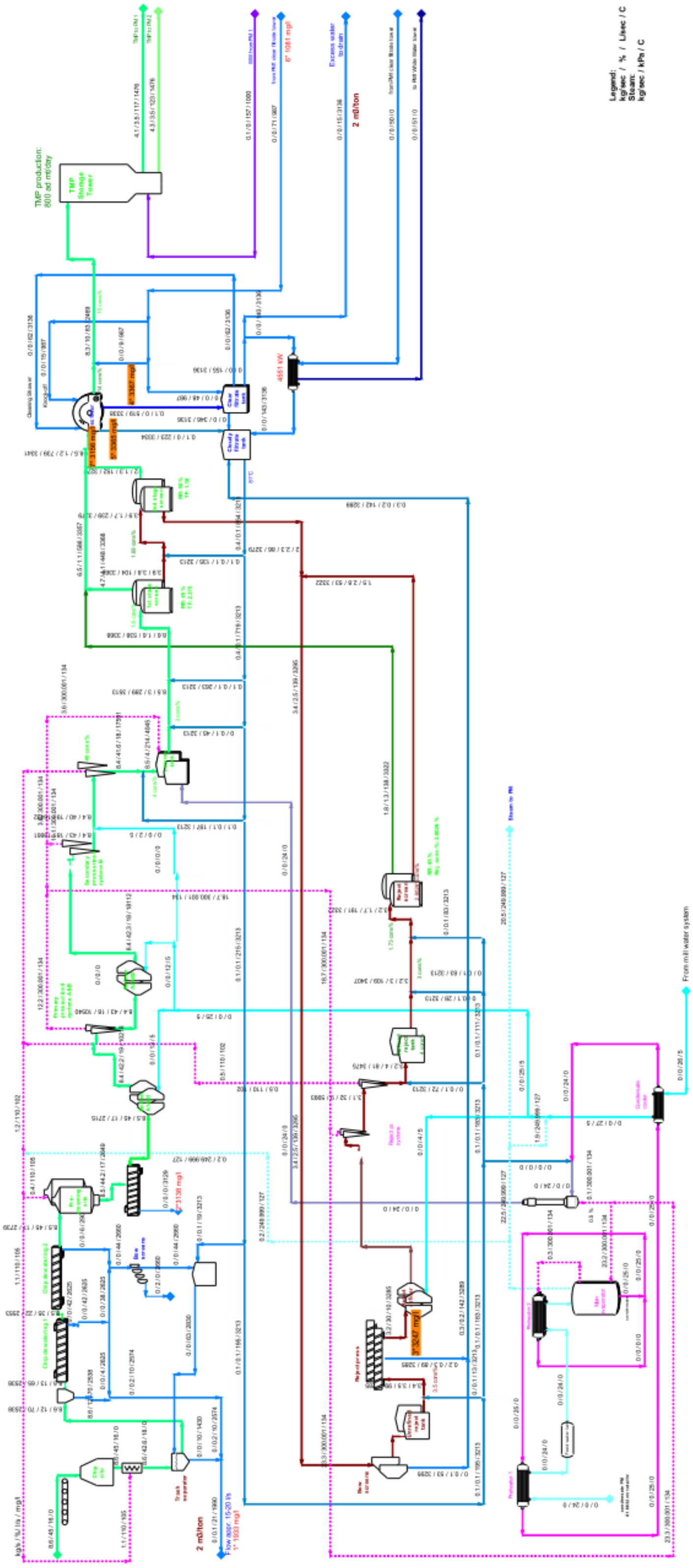
Appendix 1 Summary of the treatment methods described in chapter 4

	Treatment	DCOD removal efficiency %	COD removal efficiency %	Temp. °C	PROs (+)	CONs (-)	Water	Reference
	DAF	10...30			Moderate (30%) DCOD reduction Efficient SS removal.	Limited DCOD remov. (Inefficent in anionic trash remov.) Greater COD reductions require heavy chemical dosing		Miranda et al. 2008
	But: DAF **with** coagulation -> 75% removal efficiency of *colloidal extractives (Tanase Opedal 2011)*							
Filtration	Nanofiltration (NF)				Removes almost all (88%) of the organic contaminants. Ultraclean permeate (replaces fresh water and even high pressure water).	Limited flux capacity Fouling of the membrane Requires efficient pretreatment -> Hence expensive. Practical applications limited Requires concentrate treatment		Nuortila-Jokinen et al. 2004
Filtration	NF bloggaging can be decreased and efficiency of DCOD removal increased with , e.g. chemical treatment, biological treatment, and ozonation Ceramic membranes durate the high temperatures of TMP							
Filtration	Ultrafiltration, 10kDaltons	35	-	50	-Removes slime problems. -The permeate suits for paper machine shower water.	Limited flux capacity Fouling of the membrane Limited DCOD removal Requires concentrate treatment	TMP, BCTMP white water	Tardif & Hall 1997
Filtration	Ultrafiltration, 100kDaltons	20	-	50	-Removes slime problems. -The permeate suits for paper machine shower water.	Limited flux capacity Fouling of the membrane Limited DCOD removal Requires concentrate treatment	TMP, BCTMP white water	Tardif & Hall 1997
Biological treatment	MBR, 75kDaltons, HRT 17h,67h	77,72	-	55	These biological treatment methods remove well carbohydrates and lignan (COD inTMP) and bacteria especially if temperature is moderate). **BUT** removal of lignin and extractives COD in DIP)is poor in biological treatment		TMP, BCTMP white water	Tardif & Hall 1997
Biological treatment	Aerobic MBBR. HRT 6h	76		50			TMP white water	Widsten et al. 2004
Biological treatment	Anaerobic MBBR	40-55	-	55		Applications missing	TMP white water	Jahren et al. 1999
Biological treatment	Anarobic hybrid reactor (UASB + filter)	60-70	-	55			TMP white water	Jahren et al. 1999
Biological treatment	SBR, HRT 48h	9	-	50			TMP, BCTMP white water	Tardif & Hall 1997
Biological treatment	SBR, HRT 48h	63-76	-	20-45		Note: Low temperature	TMP, BCTMP white water	Tardif & Hall 1997
Biological treatment	SBR + UF, HRT 48h	94-84	-	30-40		Note: Low temperature	TMP, BCTMP white water	Tardif & Hall 1997
Biological treatment	Combined anaerobic/aerobic (anaerobic fluidized bed reactor and aerobic suspended biofilm carrier rector)		88-93	37		Nutrient dosing is challenging Note:Low temperature	Recycled paper for pakacking mill	Alexandersson et al. 2005
Biological treatment	Combined anaerobic/aerobic (anaerobic fluidized bed reactor and aerobic suspended biofilm carrier rector)		87	55		Nutrient dosing is challenging PROs: high COD removal, tackling the buildup of volatile fatty acids, reduction of sulphate and in some cases digesting of wood resins.	Recycled paper for pakacking mill	Alexandersson et al. 2005 Hubbe 2007 a
	Combined enzymatic and fungal treatment		Reduction of: Lignans and ester bonded extractives >90%, Resin acids 40% Fatty acids 60% Carbohydrate 62-71% Lignin increased		Degrades well spesific compounds -> pretreatment for, e.g., biological treatment	Not suitable alone Practical applications are missing	TMP white water	Zhang et al. 2002
	Evaporation		97			High consumption of energy Large space requirement Problem with low-boiling organic material		Gartz 1996
	Wet air oxidation (200°C,10bar)		70					Molina 2002

Appendix 2 Fitting curve

Appendix 3 TMP model



Appendix 4 PM model